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Nos. 11 and 12

STUDIES IN MINERALOGY

Dedicated to

EDWARD HENRY KRAUS

Dedicated by his colleagues and friends to Edward Henry Kraus, Professor Emeritus of Crystallography and Mineralogy, and Dean Emeritus of the College of Literature, Science and the Arts of the University of Michigan, on the occasion of his eightieth birthday.



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EDWARD HENRY KRAUS

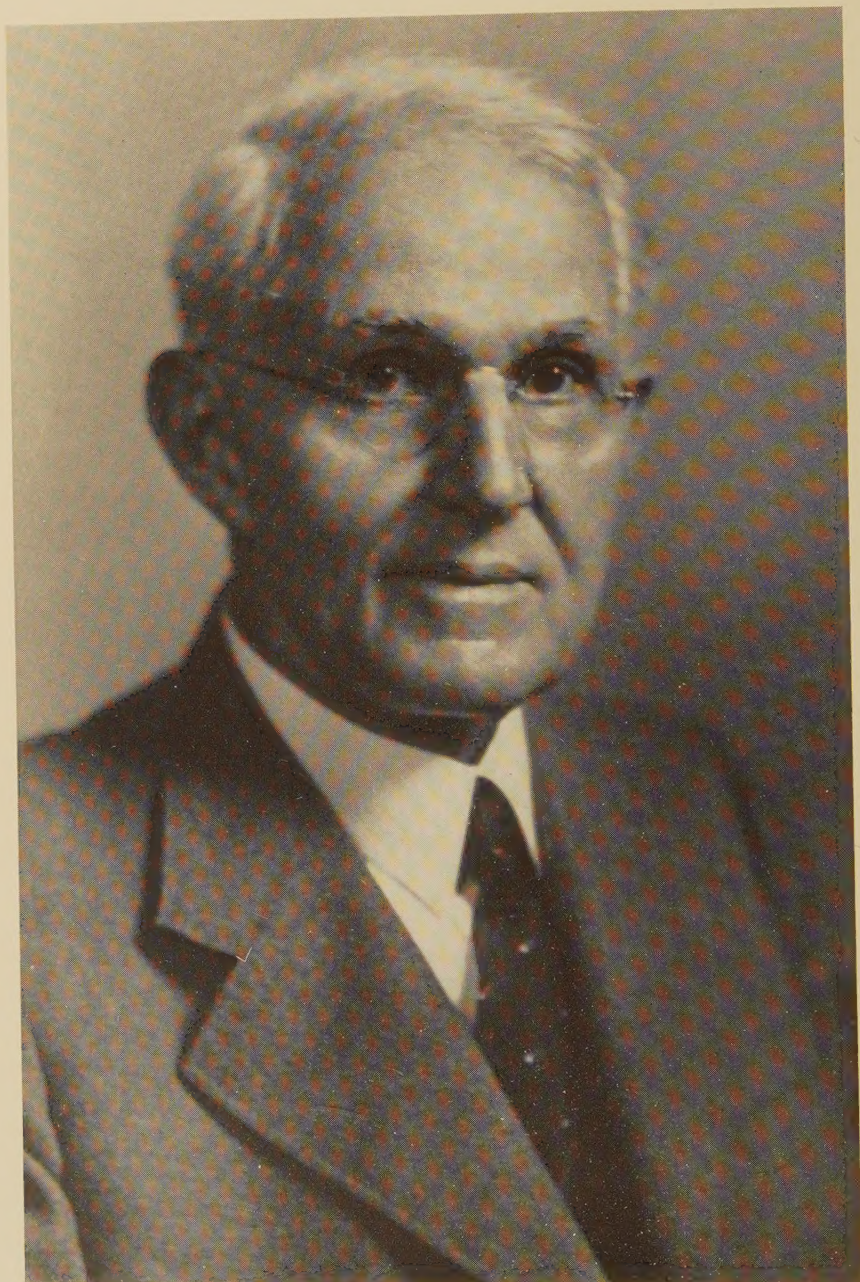
Professor Emeritus of Crystallography and Mineralogy, and Dean Emeritus of the College of Literature, Science and the Arts of the University of Michigan, by his colleagues and friends, on the occasion of his eightieth birthday.

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THE AMERICAN MINERALOGIST

JOURNAL OF THE MINERALOGICAL SOCIETY OF AMERICA

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EDWARD HENRY KRAUS*

WALTER F. HUNT

This number of *The American Mineralogist* is dedicated by his colleagues and friends to Edward Henry Kraus on the occasion of his eightieth birthday in recognition of, and deep appreciation for, his numerous services to both the science of mineralogy that is his special field of scientific interest, and to the University of Michigan which he has served so faithfully for over forty years. In modern times there are few instances in which a single individual has been called upon to undertake so many varied and difficult tasks with such fruitful results.

His success in the various fields may be attributed to a rare combination of unusual personal characteristics by means of which he was able to translate desired goals into accomplished deeds. To those who have had the privilege of being closely associated with him, he will always be known as a stimulating teacher, a painstaking investigator, an able administrator and successful author of college texts that through the years have demonstrated lasting vitality. For one who was interested in so many worthwhile projects it is impossible in a short introduction to enumerate and evaluate all his numerous activities. Instead in the limited space available only a brief outline of some of the outstanding accomplishments will be recorded.

Edward H. Kraus was born in Syracuse, New York, Dec. 1, 1875, and received his early education in the schools and University of that city, receiving his B.S. in 1896 and M.S. in 1897. His alma mater on two occasions has paid tribute to his leadership in the fields of Science and Education through the granting of two honorary degrees, Doctor of Science in 1920 and Doctor of Laws in 1934. Shortly after completing his studies at Syracuse University he spent two years in Professor Paul Groth's laboratory at the University of Munich, Germany. Here he pursued advanced work in crystallography, optics and in the cognate subjects of geology and chemistry, and received the degree of Ph.D. in 1901. This degree was renewed by the University of Munich on Sept. 15,

* Contribution from the Department of Mineralogy and Petrography, University of Michigan, No. 196.

1952—an unusual procedure. He returned to Syracuse and served on the faculty of that University during 1901–1902, when he was chosen as Head of the Science Department of Syracuse Central High School, a position he retained until he came to the University of Michigan as assistant professor of mineralogy in 1904. His advancement from the start was exceedingly rapid for two years later he was made junior professor and was promoted to a full professorship and director of the mineralogical laboratory in 1908. Under his leadership the department grew rapidly because of his energy, enthusiasm and foresight. He became emeritus in 1945.

In addition to being a stimulating teacher Dr. Kraus possesses rare executive and administrative abilities. He has therefore been called upon frequently to serve the University in various additional capacities: as Secretary of the Administrative Council of the Graduate School from 1908–1912; from 1911 to 1915 he served as Acting Dean of the Summer Session and from 1915 to 1933 as Dean. During this period the Summer Session became one of the foremost institutions of its kind in the country. In the College of Pharmacy he was Acting Dean from 1920 to 1923 and Dean from 1923 until 1933. In 1933 he was appointed Dean of the College of Literature, Science and the Arts, the largest single administrative unit of the University with an enrollment at that time of approximately 5000 students. Because of his manifold duties in his new position he was relieved of all formal teaching, although he continued to keep in close touch with the advances in mineralogy and frequently returned to his private office in the department where undisturbed he continued his investigations and writings.

Some of the older members will recall that Dr. Kraus was a member of the organization committee and as chairman was largely responsible for the founding of The Mineralogical Society of America. At the Albany meeting of The Geological Society of America in 1916 a small group of six decided to take some formal action as it was felt such action would stimulate greater interest in mineralogy and at the same time offer a ready outlet for the ever-increasing number of papers in this field. This small group consisted of Edward H. Kraus, Alexander H. Phillips, Frank R. Van Horn, Thomas L. Walker, Edgar T. Wherry and Herbert P. Whitlock. After considerable correspondence an organization meeting was called for December 30, 1919. At this meeting, held in conjunction with the 32nd annual meeting of the G.S.A., a group of 28 mineralogists met in the Mineralogical Museum of Harvard University and organized a new Society. The first President of the newly formed Society was Dr. Kraus, a signal honor to the leader of this small group and formal

recognition by the Society that the goal of the organization committee had been achieved.

Dr. Kraus' interest in the activity and welfare of the Society has continued unabated throughout the years. It was his suggestion made at the 10th annual meeting that it would be very helpful if the Society had means to establish awards for research and noteworthy achievements in the field of mineralogy that ultimately led to the establishment of the Roebling Medal in 1930.

Dr. Kraus is a fellow of The Mineralogical Society of America (President in 1920 and recently appointed Honorary President by the Council), The Geological Society of America since 1902, and the American Association for the Advancement of Science. He also holds membership in the American Chemical Society, Optical Society of America, American Institute of Mining and Metallurgical Engineers, Michigan Academy of Science, Arts and Letters (President in 1920), American Pharmaceutical Association, American Association of Colleges of Pharmacy (President in 1926), and for ten years (1930-1940) served on the committee on the revision of the U.S. Pharmacopea. He is an honorary fellow of the American College of Dentists and honorary member of Die Deutsche Mineralogische Gesellschaft, Die Deutsche Gesellschaft für Edelsteinkunde, the Gemological Association of Great Britain, the Gemological Institute of America and is a certified gemologist of the American Gem Society.

Although burdened for a long period by many time-consuming administrative duties, he still found opportunity to contribute liberally to mineralogical literature. His list of about 100 publications covers a wide range of subjects relating to the occurrence and origin of minerals, crystallographic forms observed on crystals, new apparatus to determine specific properties of minerals and rocks, and papers and addresses dealing with educational trends and policies. He was one of the pioneers in the study of the variation of hardness in the diamond, a subject that in recent years has become of prime importance not only in diamond cutting but in diamond drilling explorations as well. In this connection it should be mentioned that Dr. Kraus was the organizer and chairman of three Symposiums on Diamonds in 1941, 1942 and 1945.

Dr. Kraus was largely instrumental in offering constructive suggestions that resulted in the design of the Roebling medal, and he also gave the presentation addresses of four Roebling medalists: Charles Palache (1937); Paul Niggli (1947); Fred. E. Wright (1952); and William F. Foshag (1953).

In addition to his long list of papers, he is the sole author of two and senior co-author with his colleagues of three texts on Crystallography,

Tables for the Determination of Minerals, Descriptive and General Mineralogy, and Gems and Gem Materials. The last two are in their fourth and fifth editions, respectively, indicating widespread adoptions.

One of the highest honors that can be conferred by the University of Michigan on a member of its faculty came to Dr. Kraus when he was chosen the Henry Russell Lecturer in 1945. The selection of the recipient of this lectureship is made each year by the University Research Club. It was in this same year that he received the Roebling Medal from The Mineralogical Society of America. In 1954 he was selected to give the Orton Lecture before the American Ceramic Society.

While the above citations record accomplishments in the scientific field, this introduction would be wholly inadequate if it did not mention his sterling character and genuine interest in civic, church and humane activities. Uncompromising in his attitude when a wrong or an unethical act has been committed he unhesitatingly refuses to compromise for the sake of expediency—attributes inherent in a true Christian gentleman.

For the past seven years he has been President of the Humane Society of Washtenaw County, Michigan, and has exercised the same energy, enthusiasm and foresight that have been shown in other endeavors and he was largely responsible for bringing into being a "shelter" for the protection and care of animals that has been acclaimed one of the best in the country.

I am sure his numerous friends will agree with the writer that in dedicating this issue to Dr. Kraus we are paying a well merited tribute to his long and varied service in many fields. This writing finds him hale, hearty and vigorous, which bespeaks continued interest in the welfare of the Society. It is the hope that the Society will continue to receive the benefits of his wise counsel for many years to come.

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TAVORITE AND BARBOSALITE, TWO NEW PHOSPHATE MINERALS FROM MINAS GERAIS, BRAZIL*

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ABSTRACT

Two more new phosphate minerals—tavorite and barbosalite—have been discovered in the Sapucaia pegmatite mine in Minas Gerais, Brazil. Three other minerals recently described were named frondelite, faheyite, and moraesite. The Sapucaia pegmatite is granitic in composition, is zoned on the basis of texture and mineral composition, and has had a significant production of muscovite and beryl.

Tavorite and barbosalite are intimately intergrown secondary phosphate minerals that occur with many other phosphate minerals in the pegmatite, such as heterosite, ferrisicklerite, hureaulite, vivianite, strengite, metastrengite, childrenite, variscite, frondelite, faheyite, moraesite, triphylite, montebrasite, roscherite, and apatite. Other accessory minerals are spodumene, beryl, tourmaline, and sulfides. Quartz, perthite, albite, and muscovite are the essential minerals of the rock.

Tavorite is a hydrous lithium ferric phosphate, the ferric analogue of montebrasite with which it is isostructural. It is named in honor of Dr. Elysairio Tavora, Professor of Mineralogy, Universidade do Brazil, Rio de Janeiro. The mineral occurs as a yellow, very fine grained aggregate with a mean index of refraction of 1.807 and a specific gravity of 3.29. The chemical analysis shows the following percentages: Li_2O 7.64, FeO 2.39, MnO 1.47, Fe_2O_3 42.57, P_2O_5 39.78, H_2O^+ 5.76, and H_2O^- 0.40. The formula, as derived from the chemical analysis, is $(\text{Li}_{0.90}, \text{Fe}''_{0.06}, \text{Mn}''_{0.04}) \text{Fe}'''_{0.94}(\text{PO}_4)_{0.99}(\text{OH})_{1.13}$ as compared with the ideal formula $\text{LiFe}(\text{PO}_4)(\text{OH})$. X-ray powder data show principal d -spacing (in Å) at 3.045, 3.285, 4.99, 4.68, and 2.474.

Barbosalite is a hydrous ferrous ferric phosphate, the ferric analogue of scorzalite. It is named in honor of A. L. de M. Barbosa, Professor of Geology, Escola de Minas, Minas Gerais, Brazil. The mineral occurs in black nearly opaque grains and masses. Thin grain edges are dark blue green with evident pleochroism. The approximate indices of refraction are: $\alpha=1.77$ and $\gamma=1.835$ and the specific gravity is 3.60. The chemical analysis, recalculated to 100 per cent after subtracting admixed tavorite, is: FeO 13.10, MnO 2.82, Fe_2O_3 41.65, P_2O_5 37.50, and H_2O 4.93 per cent. Its ideal chemical formula is $\text{Fe}''\text{Fe}'''_2(\text{PO}_4)_2(\text{OH})_2$. X-ray powder data indicate principal d -spacings (in Å) at 3.361, 3.313, 4.84, 3.239, 3.160, and 2.327. The mineral is structurally identical with a synthesized compound described by Gheith as ferrous ferric lazulite and both are closely related to, but have larger cell size than, scorzalite.

Tavorite and barbosalite are examples of complete substitution of trivalent iron for aluminum in known mineral structures.

INTRODUCTION

Tavorite and barbosalite are two new phosphate minerals from the Sapucaia pegmatite mine, Minas Gerais, Brazil. Three others—frondelite, faheyite, and moraesite—have been described in earlier issues of this journal (Lindberg, 1949; Lindberg and Murata, 1953; and Lind-

* Publication authorized by the Director, U. S. Geological Survey.

berg, Pecora, and Barbosa, 1953). These accounts are preliminary to a more detailed description, in preparation, of the mineralogy and structure of the pegmatite. A summary of the present paper was published in *Science* (Lindberg and Pecora, 1954).

The Sapucaia pegmatite mine is in the municipio of Galilea, formerly a part of Conselheiro Pena, in the Rio Doce valley region in eastern Minas Gerais. This mine, a substantial producer of mica and beryl, was mapped and studied in the period 1943–1945 by Messrs. Pecora and Barbosa, participants in a joint field program of pegmatite investigations in Brazil by the U. S. Geological Survey and the Departamento Nacional da Produção Mineral (D.N.P.M.) of Brazil. Suites of mineral specimens collected during those visits were examined in Rio de Janeiro and later were turned over to Mrs. Lindberg for a more detailed mineralogical study. The original collections were augmented by additions in 1950–1953 from other sources. Type material of both tavorite and barbosalite have been deposited with the U. S. National Museum, Washington, D. C. (U.S.N.M. 106, 842) and with the Museu Nacional of the D.N.P.M., Rio de Janeiro.

GEOLOGIC RELATIONS

The granitic pegmatite at the Sapucaia mine is oval shaped in plan and internally well zoned (Pecora, et al., 1950, p. 254). The essential minerals are quartz, perthite, muscovite, and beryl. Phosphate minerals are abundant in the central part of the pegmatite. Several tons of discarded phosphate material are scattered in the mine waste of the dump.

Triphylite is the principal phosphate mineral, and heterosite is its chief alteration product. Other phosphate minerals, in addition to tavorite and barbosalite, are frondelite, hureaulite, vivianite, faheyite, childrenite, apatite, roscherite, strengite, metastrengite, variscite, ferrisicklerite, montebrasite, and moraesite.

The central part of the pegmatite, where open-pit operations are conducted for recovery of beryl, is essentially composed of giant-sized perthite masses containing numerous irregular books of "reeved" and "fish-tailed," light-colored muscovite; an irregular framework of quartz; several elongate, fluted masses of beryl; and a ramiform veinlike mass of triphylite that is intricately veined by dark purple heterosite. Several minerals locally intergrown with unaltered triphylite are quartz, muscovite, albite, sphalerite and other sulfides, tourmaline, and montebrasite.

The alteration of triphylite is characterized by the formation of heterosite and many other secondary phosphate minerals. It has not yet been established which minerals were formed by hydrothermal alteration and which by weathering. The principal feature of the alteration is a

crude mineral zoning, well demonstrated by abundant hand specimens and illustrated schematically in Fig. 1. Massive, unaltered triphylite is separated from massive heterosite and ferrisicklerite by a porous, altered triphylite zone whose spongelike cavities contain terminated crystals of colorless hureaulite, crystalline aggregates of blue vivianite, and crystalline aggregates of black barbosolite. Most of the barbosolite and tavorite, however, is found in a zone between the heterosite and porous

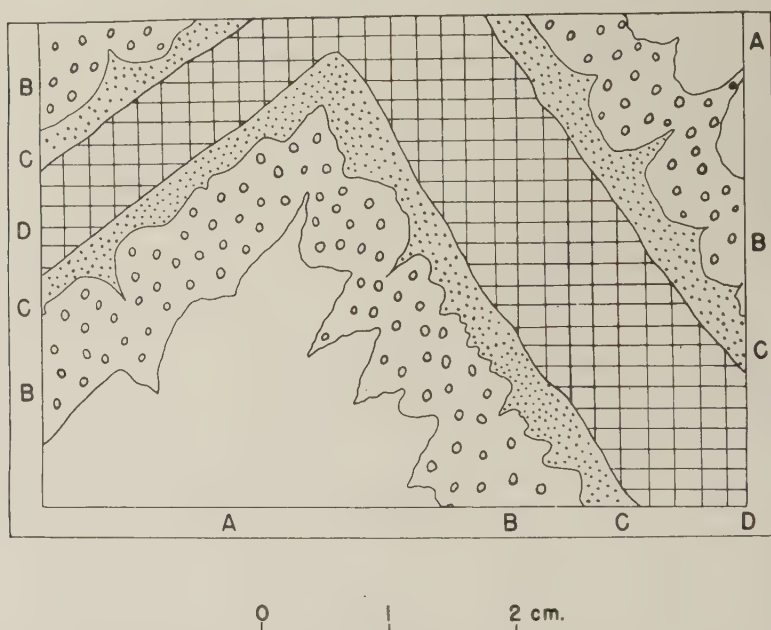


FIG. 1. Idealized sketch showing zones of secondary phosphate minerals in triphylite. A, unaltered triphylite; B, porous, altered triphylite with cavities containing colorless hureaulite crystals, crystalline aggregates of blue vivianite, and crystalline aggregates of black barbosolite; C, fine-grained blue-green zone containing essentially black barbosolite, yellow tavorite, and intermediate alteration products; D, massive purple heterosite with some brown ferrisicklerite. See Fig. 2 for details of thin section.

triphylite. A photomicrograph showing the fabric of the alteration zones is reproduced in Fig. 2.

Neither tavorite nor barbosolite has been found as single crystals, although the latter occurs as very fine grained crystal aggregates in cavities. Tavorite not uncommonly occurs relatively free of impurity, but it also occurs admixed with barbosolite in such varying proportions that it presents a wide color range in specimens from yellow to yellow green, grass green, and dark green.

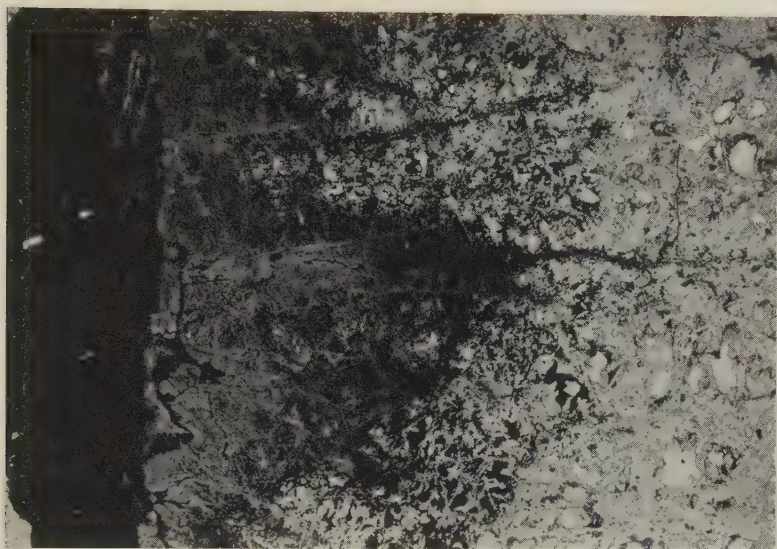


FIG. 2. Photomicrograph (plane polarized light, original dimensions 16×11 cm) showing details of alteration zoning. From left to right: heterosite (black), tavorite (dark gray), barbosalite (black), and porous, altered triphylite (white). The porous altered triphylite is lined with a network of hureaulite crystals, the shape of which is easily visible in contact with barbosalite.

TAVORITE

Tavorite (ta'-vor-ite) is a hydrous lithium ferric phosphate, the ferric analogue of montebbrasite, with iron substituting for aluminum. The ideal formula is $\text{LiFe}'''(\text{PO}_4)(\text{OH})$. The mineral is named for Dr. Elysiario Tavora, Professor of Mineralogy at the Universidade do Brasil, Rio de Janeiro.

Distribution

Tavorite occurs principally as discontinuous, greenish-yellow veinlets and disseminations, less than 5 mm. in width, at or near the contact of heterosite and barbosalite. It also occurs as a microscopic network (see Fig. 2) veining heterosite, ferrisicklerite, and barbosalite. Scattered flakes of tavorite are sparsely distributed along cleavage cracks in altered triphylite. Tavorite intimately replaces both barbosalite and crystals of hureaulite.

Physical properties

Tavorite is greenish yellow with a mean index of refraction as measured on aggregate mineral grains from vein material of 1.807. Flakes of tavorite scattered through triphylite have lower indices of refraction,

probably due to an excess of adsorbed water. The very fine grained habit prevented determination of the optical constants. The specific gravity is 3.288, as determined by means of an Adams-Johnston pycnometer of fused silica. The isomorphous and isostructural relationships of tavorite and montebrasite, as indicated by comparison of their formulas and powder photographs, suggest that tavorite is triclinic.

Chemical composition

The sample of tavorite that was analyzed was determined by grain counts to contain less than 1 per cent of impurity, principally barbosolite but also hureaulite and heterosite. The sample was purified by hand picking of large grains, followed by crushing to free the intergrowths, which were removed by the Frantz isodynamic separator and by heavy liquids (methylene iodide). Clerici solution is unsuitable because of chemical attack.

The chemical analysis of tavorite is given in Table 1, column 2, where it may be compared with the calculated theoretical composition, column 1.

The mineral is essentially a hydrous lithium ferric phosphate. Its formula, as calculated from its chemical analysis (making one oxygen equivalent to 0.566) is: $(\text{Li}_{0.90}\text{Fe}''_{0.06}\text{Mn}''_{0.04})\text{Fe}'''_{0.94}(\text{PO}_4)_{0.99}(\text{OH})_{1.13}$. The ideal formula can be expressed as $\text{LiFe}'''(\text{PO}_4)(\text{OH})$, comparable to that of montebrasite, $\text{LiAl}(\text{PO}_4)(\text{OH})$.

Tavorite yields water in a closed tube and gives a red (lithium) flame test. The mineral is easily soluble in hot dilute HCl and is slowly soluble in hot dilute HNO_3 and H_2SO_4 .

X-ray powder data

X-ray powder *d*-spacing data for tavorite are given in Table 3, column 2. The pattern is similar to but not identical with that of montebrasite from the Sapucaia pegmatite (Table 3, column 1). The chief difference between the patterns is in cell size, but differences in intensities of corresponding lines also exist. The *d*-spacings for tavorite and montebrasite are arranged by visual inspection so that reflections from provisionally equivalent planes are in the same line. Indexing the powder photograph may produce refinements.

BARBOSALITE

Barbosolite is a hydrous ferrous ferric phosphate, the ferric equivalent to scorzalite, with trivalent iron substituting for aluminum. Its ideal formula is $\text{Fe}''\text{Fe}'''_2(\text{PO}_4)_2(\text{OH}_2)$. It is isostructural with scorzalite and the synthesized compound prepared in the laboratory of J. W. Gruner

TABLE 1. CHEMICAL ANALYSIS AND RATIOS OF TAVORITE
Analyst: M. L. Lindberg

	Theoretical composition	Chemical analysis ¹	Ratios	Metal equivalent	Oxygen equivalent
LiO ₂	8.54	7.64	0.2557	0.5114	0.2557
FeO		2.39	0.0333	0.0333	0.0333
MnO		1.47	0.0207	0.0207	0.0207
Fe ₂ O ₃	45.70	42.57	0.2666	0.5331	0.7997
P ₂ O ₅	40.61	39.78	0.2802	0.5604	1.4011
H ₂ O+	5.15	5.76	0.3197	0.6394	0.3197
H ₂ O—		0.40			
Total	100.00	100.01			2.8302

Specific gravity 3.288.

Spectrographic analysis by J. D. Fletcher, U. S. Geological Survey, shows, in addition
0.0X Mg, Si, Na, Ca, Zn, Al
0.00X Cu
0.000X Cr, Be

Formula: $(\text{Li}_{0.90}\text{Fe}''_{0.06}\text{Mn}''_{0.04}\text{Fe}'''_{0.94}(\text{PO}_4)_{0.99}(\text{OH})_{1.13}$

¹ Conventional methods were used to complete the analysis. Lithia was determined by a modified J. Lawrence Smith method. The alkali fusion was leached with water repeatedly until the washings gave no test for lithia with the hand spectroscope. The insoluble matter was then filtered off, ignited at a very low heat, powdered and mixed with additional NH₄Cl and CaCO₃, and a second fusion was made. This was again leached with water repeatedly until the washings gave no test for lithia. The insoluble matter was then dissolved in HCl and tested—before discarding—for lithia, which was absent. The (NH₄)₂CO₃—NH₄OH precipitation of CaCO₃ was dissolved and reprecipitated two additional times to free Li₂CO₃. The combined lithium salts were then evaporated to dryness and the ammonia salts driven off. Lithium was then converted to the sulfate and weighed; a correction was later made for a small amount of calcium precipitated as the oxalate. Spectrographic results (0X%Na) eliminated the need for a separation of sodium and lithium.

and described as monoclinic ferrous ferric lazulite by Gheith (1953). The mineral is named for A. L. de M. Barbosa, Escola de Minas, Minas Gerais, Brazil.

Distribution

Barbosalite occurs principally as a very fine grained, dark blue-green layer between heterosite and porous triphylite. The contact with heterosite is well defined, but with the porous triphylite it is gradational, locally extending irregularly or along cleavage cracks into unaltered triphylite. The width of the layer ranges from a few millimeters to about 1 cm. In the cavities, barbosalite occurs as a massive material deposited among hureaulite crystals or as a thin coating of very fine crystalline

aggregates on hureaulite crystals. The cavities near the heterosite contain the most barbosolite. The contacts between hureaulite and barbosolite are sharp, suggesting little or no reaction and replacement.

Physical properties

The absorption of barbosolite is so strong that in thin section the mineral is opaque. In oil immersion, very fine grains show X and Y = dark blue green and Z = dark olive green. The absorption formula is X and Y > Z. The approximate indices of refraction are: $\alpha = 1.77$, $\gamma = 1.835$, and β is above but near 1.79. Optic angle could not be determined but is presumably large. The mineral is monoclinic. Its specific gravity as determined by an Adams-Johnston pycnometer is approximately 3.60, after correction for the contained tavorite.

Chemical composition

The sample of barbosolite that was analyzed contains, by grain count, one-fifth nonopaque material, with tavorite the only contaminant identifiable by optical or x-ray methods. The sample was purified by handpicking of large grains, followed by crushing to free admixed ma-

TABLE 2. CHEMICAL ANALYSIS AND RATIOS OF BARBOSOLITE
Analyst: M. L. Lindberg

	Theoretical composition	Chemical analysis	Tavorite equivalent	Barbosolite equivalent	Barbosolite recalculated to 100 per cent	Ratios	Metal equivalent	Oxygen equivalent
LiO ₂		2.01	2.01					
FeO	18.35	10.26	0.63	9.63	13.10	0.1823	0.1823	0.1823
MnO		2.46	0.39	2.07	2.82	0.0398	0.0398	0.0398
Fe ₂ O ₃	40.79	41.81	11.20	30.61	41.65	0.2608	0.5216	0.7824
P ₂ O ₅	36.26	38.02	10.46	27.56	37.50	0.2642	0.5284	1.3210
H ₂ O	4.60	5.14	1.52	3.62	4.93	0.2736	0.5472	0.2736
H ₂ O—		0.20	0.11					
Total	100.00	99.90	26.32	73.49	100.00			2.5991
Specific gravity		3.511	3.288		3.598			

Spectrographic analysis by J. D. Fletcher, U. S. Geological Survey, shows, in addition:

0.0X Mg, Si, Na, Ca, Zn

0.00X Al

0.000X Cu

Formula: $\text{Fe}''_{0.70}\text{Mn}''_{0.15}\text{Fe}'''_{2.01}(\text{PO}_4)_{2.08}(\text{OH})_{2.10}$

terials, which were removed by the Frantz isodynamic separator, and by differential settling in methylene iodide. Clerici solution was not used, because it was observed to react with the mineral. A microsample of pure barbosolite obtained from hureaulite-filled cavities gave a negative chemical test for lithium.

The chemical analysis of the impure barbosolite sample is given in Table 2, column 2. The lithia is attributed to admixed tavorite. The proportional amounts of constituents for tavorite (column 3) are subtracted from column 2 to give the barbosolite equivalent in column 4, which is recalculated to 100 per cent in column 5. The results compare favorably with the theoretical analysis (column 1). The formula, calculated from the analysis on a basis of ten oxygens equal to 2.60 is $\text{Fe}''_{0.70}\text{Mn}''_{0.15}\text{Fe}'''_{2.01}(\text{PO}_4)_{2.03}(\text{OH})_{2.10}$. The ideal formula can be expressed as $\text{Fe}''\text{Fe}'''_2(\text{PO}_4)_2(\text{OH})_2$ comparable to that of scorzalite $\text{Fe}''\text{Al}_2(\text{PO}_4)_2(\text{OH})_2$.

Barbosolite yields water in a closed tube. It is slowly soluble in hot dilute HCl and is insoluble in dilute HNO_3 and H_2SO_4 . It reacts slowly with alkali solutions and is attacked by Clerici solutions.

X-ray powder data

X-ray powder *d*-spacing data for a small sample of barbosolite free of impurity are given in Table 3, column 4; the corresponding powder pattern is shown in Fig. 3, film 4. The data for the analyzed sample of barbosolite, which contains admixed tavorite, are given in column 3; the corresponding pattern is film 3. Data and patterns for montebrasite, tavorite, and scorzalite are given in the same table and figure. For the pairs of isostructural minerals (1) montebrasite and tavorite and (2) scorzalite and barbosolite, data in Table 3 are arranged to present *d*-spacings from equivalent diffraction planes in the same line, and the offset in the powder patterns (see Fig. 3) illustrates differences in cell size. For the analyzed sample of barbosolite, which contains admixed tavorite, the *d*-spacings are arranged so as to indicate the contribution of barbosolite and tavorite to a given reflection, the mineral making the principal contribution in intensity is identified by a B or T.

The powder pattern of barbosolite corresponds, almost line for line, with that of scorzalite. The chief difference is in cell size, although small differences in intensities also are noted. The structural identity of barbosolite with a synthesized hydrous ferrous ferric phosphate (see Fig. 3, films 4 and 5) prepared in the laboratory of J. W. Gruner and described as monoclinic ferrous ferric lazulite by Gheith (1953) is evident. A dimorphous form of this compound was named lipscombite by Gheith (1953). Single crystal data by Katz and Lipscomb (1951) define lips-

TABLE 3. INTENSITY AND *d*-SPACING DATA FOR X-RAY POWDER PATTERNS OF MONTEBRASITE, TAVORITE, AND BARBOSALITE FROM THE SAPUCAIA MINE AND SCORZALITE FROM WHITE MOUNTAIN, CALIF.
(Fe radiation and Mn filter)

1 Montebrasite		2 Tavorite		3 Barbosalite, with admixed tavorite ¹			4 Barbosalite, free of impurity		5 Scorzalite	
<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>		<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>
2	6.05 Å	1	6.37 Å	2	B	6.33 Å	2	6.33 Å	3	6.19 Å
$\frac{1}{2}$	5.90									
2	5.15	5	4.99	1	T	4.97				
1	4.84	1	4.76	6	B	4.84	6	4.84	4	4.73
9	4.68	3	4.68	1	T	4.68				
2	3.755	2	3.95							
4	3.351	1	3.439							
4	3.285	1	3.400							
				10	B	3.361	10	3.361	10	3.248
6	3.221	2	3.323	10	B	3.320	8	3.313	9	3.204
6	3.169	9	3.285							
		$\frac{1}{2}$	3.244	4	B	3.239	6	3.239	5	3.152
				4	B	3.160	6	3.160	3	3.077
10	2.971	10	3.045	4	T	3.045				
2	2.578	1	2.655	$\frac{1}{2}$	BT	2.655	1	2.652		
				2	B	2.614	3	2.614	4	2.556
2	2.502	1	2.558	$\frac{1}{2}$	T	2.558				
$\frac{1}{2}$	2.474	1	2.542	$\frac{1}{2}$	T	2.536				
5	2.405	4	2.474	1	T	2.474				
1	2.358	1	2.441	$\frac{1}{2}$	BT	2.439	1	2.439		
				$\frac{1}{2}$	B	2.410	1	2.407	1	2.347
3	2.296	2	2.360							
$\frac{1}{2}$	2.277			3	B	2.327	4	2.327	3	2.264
2	2.210	1	2.287	2	B	2.292	3	2.292	2	2.226
4	2.137	2	2.206	$\frac{1}{2}$	T	2.208				
1	2.108									
$\frac{1}{2}$	2.058	1	2.156	$\frac{1}{2}$	T	2.152				
$\frac{1}{2}$	2.033	1	2.113	$\frac{1}{2}$	BT	2.113	1	2.108	1	2.055
				1	B ²	{2.080}	2	{2.080}	2	2.012
				1	B	{2.057}		{2.057}	$\frac{1}{2}$	1.989
3	1.969	1	2.028	2	B	2.027	3	2.027	1	1.976
$\frac{1}{2}$	1.943	1	1.998	$\frac{1}{2}$	T	1.998				
$\frac{1}{2}$	1.931	1	1.973	$\frac{1}{2}$	T	1.973				
3	1.900	2	1.938	$\frac{1}{2}$	T	1.938			$\frac{1}{2}$	1.828
				2	B	1.880	2	1.877	1	1.811
$\frac{1}{2}$	1.823									
2	1.795	$\frac{1}{2}$	1.851	$\frac{1}{2}$	T	1.854				
2	1.758	1	1.823	1	B	1.828	1	1.828	1	1.789

¹ B, for barbosalite, and T, for tavorite, indicate the mineral making the principal contribution to the intensity of a given *d*-spacing.

² { }, bracket indicates a band between 2.080 and 2.057 Å.

TABLE 3—(continued)

1 Montebrasite		2 Tavorite		3 Barbosolite, with admixed tavorite ¹			4 Barbosolite, free of impurity		5 Scorzalite	
<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>		<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>
				$\frac{1}{2}$	B	1.788	1	1.797	$\frac{1}{2}$	1.741
$\frac{1}{2}$	1.683	$\frac{1}{2}$	1.751	$\frac{1}{2}$	B	1.757	$\frac{1}{2}$	1.776		
							1	1.757	$\frac{1}{2}$	1.688
1	1.673	2	1.722	1	T	1.721	$\frac{1}{2}$	1.746	$\frac{1}{2}$	1.667
1	1.656	1	1.705	$\frac{1}{2}$	BT	1.706	$\frac{1}{2}$	1.726		
				2	B	1.681	$\frac{1}{2}$	1.708		
$\frac{1}{2}$	1.646						3	1.681	3	1.625
2	1.623	3b	1.662	3	BT	1.658	3	1.658	2	1.605
5	1.610	2	1.642	$\frac{1}{2}$	T	1.642				
1b	1.586	2	1.620	2	BT	1.623	3	1.625	2	1.578
				2	B	1.610	3	1.610	$\frac{1}{2}$	1.563
				1	B	1.584	2	1.584	3	1.541
1	1.538	$\frac{1}{2}$	1.560							
1	1.527	$\frac{1}{2}$	1.552	$\frac{1}{2}$	BT	1.553	$\frac{1}{2}$	1.550		
1	1.487	1b	1.520	$\frac{1}{2}$	T	1.520				
1	1.477									
$\frac{1}{2}$	1.465	$\frac{1}{2}$	1.501				$\frac{1}{2}$	1.476	1	1.443
2b	1.448									
				1	B	1.466	1	1.465	2	1.416
2	1.427	1	1.453	$\frac{1}{2}$	BT	1.459	1	1.458	$\frac{1}{2}$	1.411
2	1.409	2	1.437	1	BT	1.438	1	1.439	1	1.393
1	1.392	$\frac{1}{2}$	1.424							
$\frac{1}{2}$	1.369									
$\frac{1}{2}$	1.352	$\frac{1}{2}$	1.403	1	BT	1.401	$\frac{1}{2}$	1.399	$\frac{1}{2}$	1.368
$\frac{1}{2}$	1.342	$\frac{1}{2}$	1.397	$\frac{1}{2}$	B	1.389	1	1.389	1	1.356
				$\frac{1}{2}$	B	1.372	1	1.374	1	1.340
$\frac{1}{2}$	1.322	$\frac{1}{2}$	1.360	$\frac{1}{2}$	B	1.355	1	1.353	1	1.326
$\frac{1}{2}$	1.314	$\frac{1}{2}$	1.339							
4	1.291	2	1.327	$\frac{1}{2}$	T	1.328				
				1	B	1.317	$\frac{1}{2}$	1.318		
1	1.274	1	1.300	3	B	1.309	4	1.309	4	1.280
1	1.265	1	1.285	$\frac{1}{2}$	B	1.282	$\frac{1}{2}$	1.281	$\frac{1}{2}$	1.263
2	1.253	2	1.271	$\frac{1}{2}$	BT	1.271	$\frac{1}{2}$	1.271	$\frac{1}{2}$	1.246
$\frac{1}{2}$	1.215	$\frac{1}{2}$	1.238	$\frac{1}{2}$	BT	1.239	$\frac{1}{2}$	1.238		
$\frac{1}{2}$	1.205									
				$\frac{1}{2}$	B	1.229	1	1.229	$\frac{1}{2}$ b	1.998
				1	B	1.218	1	1.218		
2	1.179	$\frac{1}{2}$	1.220							
1	1.171	$\frac{1}{2}$ b	1.210							
$\frac{1}{2}$	1.163	$\frac{1}{2}$	1.197							
2	1.153	1	1.181	1	B	1.171	2	1.171	1	1.129
				1	B	1.160	2	1.160	1	1.118
				1	B	1.128	1	1.127		
$\frac{1}{2}$	1.137	$\frac{1}{2}$	1.164				1	1.107		

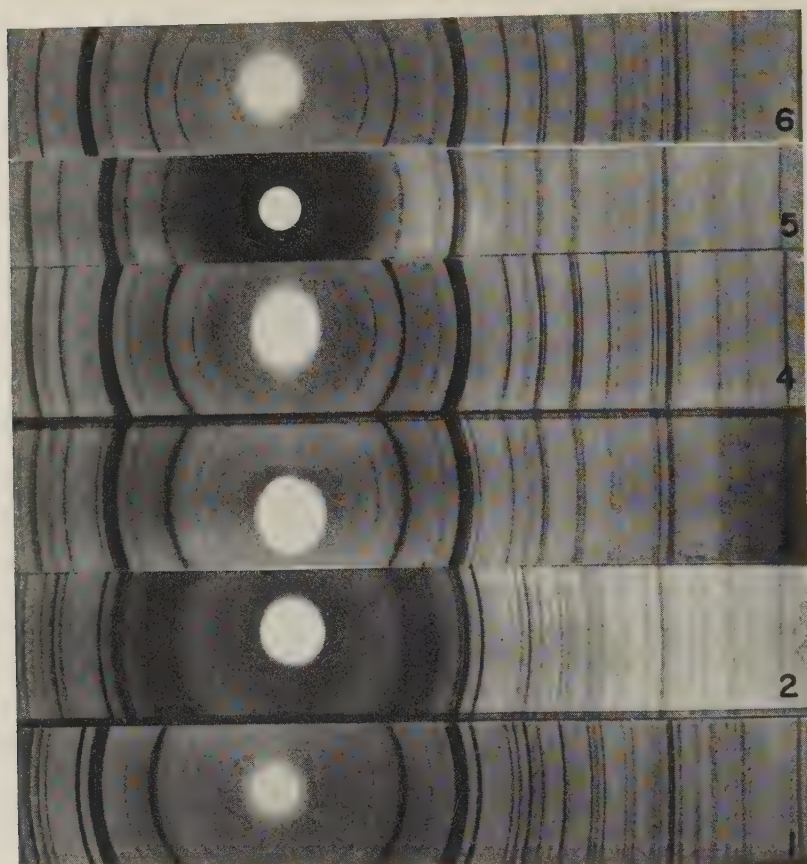


FIG. 3. Comparison of x-ray powder photographs: (1) montebrasite (Sapucaia pegmatite); (2) tavorite (analyzed sample, Sapucaia pegmatite); (3) barboselite (analyzed impure sample containing tavorite, sapucaia pegmatite); (4) barboselite (pure microsample from hureaulite-bearing cavities, Sapucaia pegmatite); (5) synthesized ferrous ferric lazulite; and (6) scorzalite (White Mountain, Calif.). The patterns are alined on the right to show differences in cell size between tavorite and montebrasite and between barboselite and scorzalite.

combite as tetragonal in symmetry. Gheith (1953, p. 612) demonstrates that the x-ray powder patterns of both compounds are similar, but that they differ from lazulite in having d -spacings corresponding to a larger unit cell.

From this correlation it is concluded that barboselite is monoclinic as are lazulite and scorzalite (Pecora and Fahey, 1950). The unit cell size of barboselite is essentially that of the synthesized ferrous ferric lazulite but larger than that of scorzalite. Minor discrepancies between the x-ray data for barboselite (this paper) and for ferrous ferric lazulite

(Gheith, 1953, p. 617) are probably explained by the fact that Gheith's patterns show the effect of unfiltered iron radiation with a consequent (1) broadening of reflection and loss of resolution, and (2) occurrence of separate reflections, representing alpha and beta radiation, of planes with the same *d*-spacing.

ORIGIN

The complex set of chemical reactions leading to the formation of the secondary phosphate mineral suite involve (1) hydration, (2) partial or complete oxidation of the ferrous and manganous ions, and (3) solution and reprecipitation of several ions to form new compounds. How much of this chemical action was the result of hydrothermal solutions and how

TABLE 4. CHEMICAL FEATURES OF TAVORITE, BARBOSALITE, AND OTHER PHOSPHATE MINERALS FROM THE SAPUCAIA PEGMATITE

Mineral	Hydration	Oxidation state		Presence of lithium
		Iron	Manganese	
Triphylite	anhydrous	ferrous	manganous	yes
Heterosite	nonessential water	ferric	manganic	no
Ferrisicklerite	nonessential water	ferric	manganous	yes
Hureaulite	acid water and water of crystallization	ferrous	manganous	no
Vivianite	water of crystallization	ferrous	manganous	no
Tavorite	hydroxyl water	ferric	manganous	yes
Barbosalite	hydroxyl water	ferrous	manganous	no
Frondelite	hydroxyl water	ferric	manganous	no
		ferric	manganic	

much the result of ground water in a humid tropical region has not as yet been established with certainty. Most of the hand specimens in our collection were obtained from within 20 meters of the surface and presumably within the range of ground-water alteration. It is our present belief, however, that much of the direct alteration of triphylite was caused by hydrothermal attack late in the consolidation history of the pegmatite.

Chemical features of tavorite, barbosalite, and associated phosphate minerals are arranged for comparison in Table 4. Triphylite is thus the only anhydrous mineral² listed, and presumably it is the original source

² In heterosite and ferrisicklerite, water is present in small and variable amounts, and is considered by Mason (1941, p. 148) to be "not constitutional, but held by forces of adsorption."

of most of the constituents, other than water, necessary to form the secondary phosphate minerals. Iron and manganese in hureaulite and vivianite are not oxidized. With respect to triphylite, hureaulite is enriched in manganese and vivianite is enriched in iron. Heterosite, on the other hand, represents a complete oxidation of iron and manganese, and ferrisicklerite a partial oxidation, with respect to triphylite. In tavorite and barbosolite the small amount of manganese present is not in the oxidized state, although the iron is substantially in the ferric state. Barbosolite and frondelite contain approximately the same amount of iron plus manganese, but frondelite is deficient in phosphate and high in hydroxyl with reference to barbosolite.

Of the minerals listed in Table 4, the relations of which are illustrated in Figs. 1 and 2, tavorite is certainly the youngest to have formed and barbosolite the next to youngest. Late in the alteration history, therefore, lithium was available and utilized to form tavorite by solutions attacking many of the earlier formed minerals. Whether this lithium was obtained by direct alteration of triphylite or its intermediate product ferrisicklerite cannot be established. The concentration of tavorite and barbosolite near the heterosite-ferrisicklerite alteration zone would strongly favor their formation through continued alteration of the intermediate products rather than from triphylite itself.

Fractures coinciding with cleavage directions of triphylite and heterosite have played an important role in guiding the development of the alteration products. This favorable physical relation applies to both the hydrothermal and weathering stages of alteration.

Chemical and mineralogical investigations of our suite of specimens are still in progress, and further information on the paragenesis of the secondary phosphate minerals will no doubt be revealed. Current studies of similar phosphate minerals from other granite pegmatites in this and other countries will contribute much to our understanding of the complex alterations involved. Much of the material is, however, so admixed and so difficult to identify and purify, that progress is unfortunately a slow affair.

PROBLEM OF NOMENCLATURE

The discovery of tavorite and barbosolite extends our knowledge of the natural substitution of ferric ions for aluminum in two different mineral structures. New mineral names are justified in both.

In the lazulite mineral group, three or four ideal end members can now be accepted as naturally occurring compounds. The substitution of ferrous ions for magnesium in lazulite results in the formation of scorzalite (Pecora and Fahey, 1950), and the additional substitution of ferric

ions for aluminum results in barbosalite. The fourth member of the group, as yet undiscovered, would be a hydrous magnesium ferric phosphate. A hydrous manganous ferric phosphate, also not yet discovered, may be predicted. Intermediate compositions within the mineral group can be conveniently designated by use of adjectival modifiers (Schaller, 1930). The synthesized monoclinic ferrous ferric lazulite described by Gheith (1953) would be analogous to barbosalite.

Tavorite represents the ferric analogue of montebrasite, and both are here accepted as the ideal end members with hydroxyl ions present instead of fluorine. Excess of fluorine over hydroxyl, as in amblygonite, denotes further chemical variation in the mineral group. Tavorite, montebrasite, and amblygonite are, then, three different members of the amblygonite mineral group. Adjectival modifiers can denote intermediate compositions.

ACKNOWLEDGMENTS

The authors are indebted to several individuals who have contributed aid or material during these investigations. E. R. Swoboda, Robert Greenwood, and Emerson I. Brown provided hand specimens from the Sapucaia pegmatite to augment the original collections of Pecora and Barbosa. John Gruner of the University of Minnesota courteously supplied two x-ray films of synthesized phosphates for comparison with barbosalite. Mary E. Mrose of the U. S. Geological Survey, who is currently engaged in a study of tavorite and other phosphates from the Fletcher quarry, North Groton, N. H., kindly compared specimens and x-ray powder photographs of tavorite from Brazil with those from her locality. Janet Fletcher of the U. S. Geological Survey provided qualitative and quantitative spectrographic analyses of tavorite and barbosalite.

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REDESCRIPTION OF THE SINGLE LAYER STRUCTURE OF THE MICAS

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ABSTRACT

It can be shown that the structure of single layer micas described by Hendricks (1939) as "monoclinic hemihedral," space group C_2^3-Cm , is very nearly holohedral. By adjustments in the x coordinates of some of the atoms not exceeding 0.005 and a new choice of origin at a center of symmetry all atomic coordinates can be brought into conformity with the conventional description of structures in the space group C_{2h}^3-C2/m . It is suggested that this description is preferable since no evidence is known requiring the lower symmetry previously assigned.

INTRODUCTION

In his well-known paper on polymorphism of the micas, Hendricks (1939) described what he referred to as "THE SINGLE LAYER STRUCTURE OF THE MICAS (MONOCLINIC HEMIHEDRAL)." In the summary of the paper this was again referred to as "Single layer monoclinic hemihedral" and was reported to occur with far greater frequency than any of the other six types described.

Since much emphasis is placed on the "hemihedral" character of this most frequent of mica structures it is of interest to examine the basis for assignment of the space group. On this point Hendricks made the following statement (1939, p. 734):

"There is only one way in which the simplest unit of structure can contain a portion of one mica layer. Atomic coordinates of this arrangement having the orientation b_1 of Fig. 1a are given in Table I. The structure is isomorphous with the monoclinic hemihedral point group C_s-m , the space group being C_2^3-Cm ."

TABLE I. ATOMIC COORDINATES FOR THE SINGLE LAYER STRUCTURE.
SPACE GROUP C_2^3-Cm , $\beta=100^\circ$

General Positions				Special Positions			
	x	y	z		x	y	z
4 O	.25	.25	.00	2 O	.00	.50	.00
4 Si	.02	.33	.06				
4 O	.08	.33	.22	2 (OH)	.08	.00	.22
4 Mg	.44	.33	.34	2 Mg	.44	.00	.34
4 O	.32	.17	.46	2 (OH)	.32	.50	.46
4 Si	.37	.17	.62				
4 O	.14	.25	.68	2 O	.39	.00	.68
				2 K	.45	.50	.84

Reproduced in facsimile from Hendricks, (1939, p. 735). The same figures are given in a table in *Strukturbericht VII*, p. 170.

TABLE 2. SINGLE LAYER MICA STRUCTURE

A. Atomic coordinates of Hendricks "expanded" in accordance with conventional description in space groups C_3-Cm . The boldface coordinates are those taken from table I. x coordinates in brackets are adjusted as described in text.

Positions		Positions									
$4b$	x	y	z	x	y	z	$\frac{1}{2}+x$	$\frac{1}{2}+y$	z	$\frac{1}{2}+x$	$\frac{1}{2}$
$4O$.25	.25	.00	.25	.75	.00	.75	.75	.00	.00	.50
$4Si, Al$.02	.33	.06	.02	.67	.06	.52	.83	.06	.00	.00
$4O$.08	.33	.22	.08	.67	.22	.58	.83	.22	.22	.50
$4Mg$.44	.33	.34	.44	.67	.34	.94	.83	.34	.34	.50
$4O$.32	.17	.46	.32	.83	.46	.82	.67	.46	.32	.50
$4Si, Al$.37	.17	.62	.37	.83	.62	.87	.67	.62	.68	.50
$4O$.14	.25	.68	.14	.75	.68	.64	.75	.68	.84	.84

The atomic coordinates for this structure given by Hendricks in his Table I are reproduced here in facsimile under the same number. They do indeed correspond to a structure in the space group Cm . However, in this space group, the choice of origin being taken in a plane of symmetry, its position in the x and z direction remains arbitrary. Hendricks so placed it that the base of the cell is at the level of the oxygens on the "outside" of the $(Si,Al)_4O_{10}$ sheet. Inspection of the z parameters in Table I will show that by moving the origin downward 0.16 the K atoms come to lie at the zero level, Mg's at half height and all other atoms at corresponding heights of plus and minus z .

Inspection of the x coordinates shows that an increase of 0.555 in these will bring the atoms very nearly, but not quite, into positions corresponding to the conventional description for a structure in the space group C_{2h}^3-C2/m . After this shift it is found that K atoms, Mg atoms, OH's and those O's adjacent to the Mg's depart only by plus or minus 0.005 from positions which would correspond to the higher symmetry. To the writer it seems that this slight departure from the higher symmetry arises simply from the way in which coordinates were given in the original description. They were given, as may be seen in Table I, to the nearest hundredth and so the small shift of parameters required to match the higher symmetry may be considered to be within the limits intended by Hendricks.

In support of his structure, which is truly hemihedral but nearly holohedral, Hendricks gave calculated and observed intensities for $h0l$ and $0kl$ reflections in his Tables II and III. There is good agreement of calculated intensities with observed intensities indicated qualitatively by the symbols vs, s, ms-s, ms, m, m-mw, mw, mw-w, w, vw and a. It seems unlikely that a change in coordinates of 0.005 for some of the atoms would modify calculated intensities to such an extent as to impair the agreement just mentioned. Under these circumstances it seems justified, in the absence of any observations requiring the lower symmetry, to describe the single layer mica structure in the space group C_{2h}^3-C2/m and to drop the designation "monoclinic hemihedral."

ANALYTICAL DEMONSTRATION

Detailed proof that the trifling shifts described above do indeed lead to a structure with the symmetry $C2/m$ may be given in tabular form. This has been done in Table 2. In the upper part of this table the coordinates given in Hendricks' Table I have been "expanded" in conformity with the requirements of space group C_s^3-Cm as described on page 87, vol. I, International Tables for X-Ray Crystallography, 1952. In brackets under some of these figures are entered x coordinates ad-

justed as follows: for Mg increased by 0.005, for K, OH and O's adjacent to Mg decreased by 0.005. In the lower part of the table the expanded and adjusted coordinates have been modified to correspond to a shift of origin by adding 0.555 to all x 's and 0.16 to all z 's. Also subscripts have been attached to the symbols of certain of the atoms for convenience in reference. It will be seen that the distribution of atoms now conforms to requirements for space group $C2/m$. Following the description on page 95 of the International Tables with origin at a center of symmetry, atomic coordinates as adjusted and modified are stated in the usual conventional fashion in Table 3. The coordinates there given correspond to those in bold face in the lower part of Table 2.

The parameter adjustments used are the smallest that can be made to

TABLE 3. ATOMIC COORDINATES FOR THE SINGLE LAYER MICA STRUCTURE IN SPACE GROUP C_{2h}^3-C2/m , STATED IN ACCORD WITH THE CONVENTIONS OF THE INTERNATIONAL TABLES FOR X-RAY CRYSTALLOGRAPHY

			x	y	z
2 K	in $2b$	$0, \frac{1}{2}, 0$			
2 Mg ₁	in $2c$	$0, 0, \frac{1}{2}$			
4 Mg ₂	in $4h$	$0, y, \frac{1}{2}$.33	
4 OH	in $4i$	$x, 0, z$.63		.38
4 O ₁	in $4i$	$x, 0, z$.055		.16
8 O ₂	in $8j$	x, y, z	.805	.25	.16
8 O ₃	in $8j$	x, y, z	.63	.33	.38
8 Si, Al	in $8j$	x, y, z	.575	.33	.22

bring atoms exactly into positions required for the higher symmetry. The shift of origin needed so that the origin will be at a center of symmetry as in the conventional description may be undertaken in various different ways since there are eight symmetry centers in the unit cell in the space group $C2/m$. An alternative shift would lead merely to an alternative description superposable by translation with that given in Table 3.

GRAPHICAL DEMONSTRATION

Finally it is possible to present the relation of the description of the single layer mica structure here proposed to that given by Hendricks in the form of a diagram. This has been done in Fig. 1. This figure shows three projections of the structure. At the right is shown the orthographic projection onto (010), at the upper left onto (001) and below this, designated (100)*, the projection onto (100) not orthographically but by lines parallel to a .

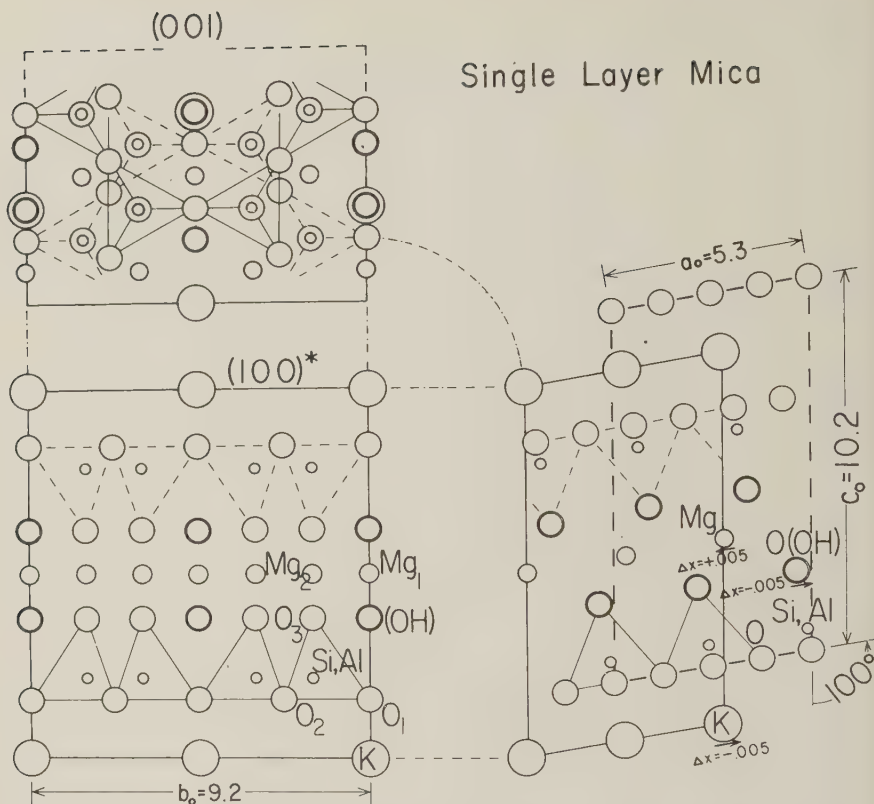


FIG. 1. Three projections to show that the single layer mica structure has the symmetry $C2/m$ after the small parameter adjustments for certain atoms shown at lower right.

At the right of the (010) projection a dimensioned cell is indicated by heavy dashed lines. Within this the atoms are plotted from the coordinates of Hendricks, the K atoms being at $z=0.84$ in this cell as given in Table I. Superposed on this is drawn the outline of a cell with the origin shifted so as to increase each x by 0.555 and each y by 0.16. The adjustments of parameter required for some of the atoms are too small to be directly discernible in the drawing. The direction and amount of these adjustments is indicated by suitable symbols under one each of the circles representing K, Mg and O(OH) in the (010) projection.

Comparison of the several projections will reveal that the K's and Mg₁'s lie at points with the symmetry $2/m$ and the Mg₂'s on two-fold axes, the entire array being in the space group $C2/m$.

(After reading the foregoing Dr. Hendricks, in a letter to Pabst dated

September 13, 1954, wrote in part as follows:—"Your analysis of the single layer mica structure is surely sound. . . . The small shift of parameters is entirely permissible within the limits of precision of our work.")

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HENDRICKS, STERLING B. (1939), Polymorphism of the micas (with optical measurements by Merrill E. Jefferson): *Am. Mineral.*, **24**, 729-771.

ADDENDUM, written May 12, 1955

Drs. J. A. Kohn and R. A. Hatch kindly furnished an excellent specimen of the synthetic fluorphlogopite which they recently described (*Am. Mineral.*, **40**, 10-21, 1955). The composition of this material is certainly known. The octahedral positions are fully occupied by magnesium with no substitutions. It is a single layer mica. This, if any, should be a suit-

TABLE 4. CALCULATED STRUCTURE FACTORS (F's) FOR THE SINGLE LAYER MICA STRUCTURE FOR THOSE ORDERS OF (*h*00) OBSERVABLE WITH MoK α RAYS

(<i>h</i> 00)	Hendricks' parameters	Modified parameters	Difference
200	100.69	100.82	0.13
400	6.58	6.75	0.17
600	7.64	8.43	0.79
800	5.99	7.48	1.49
10.00	21.19	22.01	0.82
12.00	9.85	10.16	0.31
14.00	29.34	31.17	1.83
		Sum	5.54
		Ratio of sums	2.97/100

able material for the observation of *h*00 intensities which depend on the *x* coordinates alone. Unfortunately only 200 was observable with Mo radiation, all higher orders to 1400, the last within range, being below the limit of detectability because of unfavorable influence of the L. & P. and "temperature" factors. With copper radiation only three orders of *h*00 are within range. With 200 just fully blackened on the film, 400 is not detectable and 600 is barely discernible. This agrees with the intensity observations of Hendricks which are compared below with the calculated intensities, absorption and "temperature" corrections being omitted and the calculated intensity for 200 taken arbitrarily as 100:—

	200	400	600
<i>I</i> _{obs.} Hendricks (1939, Table II)	vs	a	vw
<i>I</i> _{calc.} Hendricks' parameters	100	0.16	0.31
<i>I</i> _{calc.} modified parameters	100	0.17	0.38

It is customary to test parameters by means of a "reliability index" derived from the observed and calculated structure factors. Table 4 shows the structure factors of even orders of $h00$ up to $h=14$ for the single layer mica structure with Hendricks' parameters and with the modified parameters. The "ratio of sums" given at the foot of the table has the form of a "reliability index." Its value is much lower than is generally obtained in even the most precise crystal structure determinations.

THE CRYSTALLOGRAPHY OF "COESITE"*

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ABSTRACT

The high pressure form of SiO_2 known as "coesite" or "silica C" is monoclinic, space group Cc or $C2/c$. However, it is dimensionally hexagonal, with $a_0=c_0$ and $\beta=120^\circ$. Crystal measurements in general are very poor, but the x -ray data are excellent, and give the following results: $a_0=7.23 \text{ \AA}$, $b_0=12.52 \text{ \AA}$, $c_0=7.23 \text{ \AA}$; $d_{001}=d_{100}=d_{020}$. Two types of twinning are found, (100) and (021), chiefly based on x -ray results rather than morphology. All twin reflections either coincide with reflections of different hkl , or occupy forbidden positions. If untwinned as well as twinned crystals had not been available, it is doubtful if the space group assignment could have been made.

Through the courtesy of Dr. N. W. Thibault, Assistant Director of Research and Development, Norton Company, Worcester, Mass., the writer was provided with a sample of the new high pressure form of SiO_2 (Coes, 1953) which was named "coesite," but since it has not been found in nature, the alternative name "silica C" was also proposed (Sosman, 1954). This material was prepared in the Research Laboratories of the Norton Company. It is extremely interesting, not only as an additional polymorph of SiO_2 , but also because of some unusual crystallographic features.

The material is colorless and transparent. A few individual crystals are found with simple forms which suggest gypsum crystals. Others are more complex, with no conspicuous zone development. Much of the material is in the form of aggregates of extremely small crystals less than 0.1 mm. in length. The maximum dimension found on the crystals used in this study was 0.6 mm., and most were less than 0.4 mm. Great difficulty was encountered in mounting the crystals, and many were lost at various stages of measuring and x -raying. Those resembling gypsum were easily oriented, but for the others the orientation could in many cases be determined, if at all, only after measuring the angles.

The usual procedure was to sketch the crystals in various positions under high power binoculars. Because of the transparency, it was difficult to see the outline of an individual face unless it was oriented so as to reflect light. After mounting under a binocular microscope, the crystal was transferred to an optical goniometer and an attempt made to correlate the measured angles with the sketches. If successful, the crystal was then transferred to the x -ray goniometer. Although the crystals appear brilliant, there is some rounding of the faces, and the optical goniometer measurements were usually of poor quality. It is very doubtful if such measurements alone would have been sufficient to determine the sym-

* Contribution from Department of Mineralogy, University of Michigan, No. 188.

metry or the twin laws. Some faces could not be identified with certainty. Every crystal examined showed (010), usually as the largest form, and at least some faces of the prism (130). Additional faces were very variable and rarely were symmetrically arranged.

Fortunately, the x -ray data were much superior to the optical measurements. Excellent Weissenberg and precession photographs were obtained. These give accurate cell dimensions and the space group, and in addition reveal in some cases twinning on 100 which was not even suspected from the optical goniometric measurements. The x -ray films also show that reentrant angles observed on some crystals are caused by twinning on (021).

The x -ray data verify the monoclinic character suggested by the gypsum-like crystals, but also show that while monoclinic in symmetry, the crystals are dimensionally hexagonal, that is, $a=c$; $\beta=120^\circ$. In addition $d_{001}=d_{020}$, so that the 021 twin plane is exactly at 45° with respect to b^* and c^* , and brings them into exact coincidence on the x -ray films. The extinctions hkl with $h+k$ odd indicate an end-centered lattice, and the absence of $h0l$ reflections with l odd show that the 010 plane is a c glide plane. There is no x -ray evidence to distinguish between the two space groups Cc and $C2/c$, and the morphological data are too poor to allow a choice to be made.

X-RAY DATA
Cu $K\alpha=1.5418 \text{ \AA}$

Extinctions	
$a_0=7.23 \text{ \AA}$ $b_0=12.52 \text{ \AA}$ $c_0=7.23 \text{ \AA}$	hkl missing with $h+k$ odd hence C lattice.
$\beta=120^\circ$	$h0l$ missing with l odd hence 010 is a c glide plane.
$d_{100}=d_{001}=d_{020}$ Cell volume 536 \AA^3	Twinning on (100) and (021) revealed by Weissenberg photographs.

Goniometric measurements on six crystals gave the data in the following table. The quality of most of the signals was very poor. The calculated values are based on the unit cell dimensions.

Many of the crystals are flattened parallel to (010), and most of these have a common direction of elongation, which is chosen as the c axis. Since with an angle β of 120° , pairs of faces such as (001) and $\bar{1}01$, or (011) and $\bar{1}11$, have the same ρ angles, they cannot be distinguished morphologically, and consequently there is a dual choice for the a axis, each with the same value of β . However, x -rays easily make a distinction.

COESITE. MONOCLINIC; m OR $2/m$

$$a:b:c=0.577:1:0.577; \beta=120^\circ. p_0:q_0:r_0=1.0:0.5:1$$

$$p_0'=1.1547, q_0'=0.5773, x_0'=0.5773$$

	Form	No. times obs.	Observed range		Calculated	
			ϕ	ρ	ϕ	ρ
c	001	2	89°50'–90°30'	29°45'–30°14'	90°00'	30°00'
b	010	all xls.	0 00	90 00	0 00	90 00
i	130	all xls.	33 41 –34 10	89 52 90 10	33 42	90 00
m	110	2	62 05 –64 03	89 35 90 30	63 26	90 00
w	011	3	44 49 –46 35	38 45 –39 48	45 00	39 15
v	021	2	@ 25°	@ 52°	26 34	52 14
D	$\bar{1}01$	2	–89 34 –90 29	29 46 –30 15	–90 00	30 00
r	111	2	71 26 –71 45	61 20	71 34	61 18
R	$\bar{1}\bar{1}1$	5	–44 49 –46 20	38 45 –39 50	–45 00	39 15

One choice gives an end-centered lattice, the other a body-centered lattice. The former has been used for the description of coesite.

There is no significant deviation from the value of 120° for β on either the Weissenberg or precession photographs, nor is there any detectable difference in the values for a_0 and c_0 . The 120° angle and the dimensional equality of a and c means that there is a third direction bisecting the angle between a and c which is likewise equal. Thus the zero level Weissenberg, with rotation about the b axis, shows three central lattice lines 60° apart, all with the same spacings. However, both missing reflections and variations in intensities definitely reveal the absence of a six fold axis of symmetry. The true monoclinic character is most clearly revealed in the upper level photographs, which have only a two fold axis of symmetry. The upper levels also definitely locate the c^* direction, and hence the a axis. Figure 1 shows the reciprocal lattice for the 0, 1 and 2 levels for this orientation.

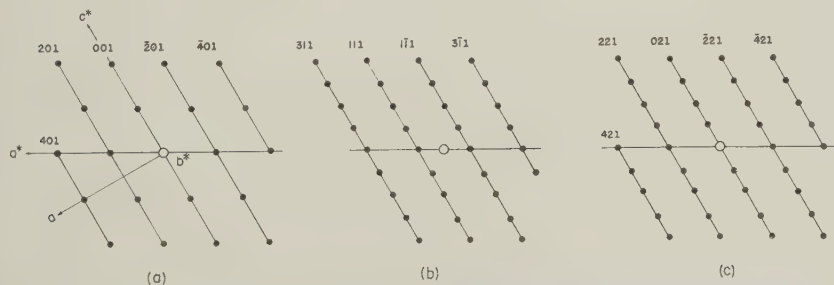


FIG. 1. Reciprocal lattice levels with rotation about the b axis. (a) 0-level, pseudohexagonal symmetry. (b) and (c) 1-level and 2-level, with symmetry C_{2i} .

MORPHOLOGY

More than a dozen crystals were observed which showed some resemblance to gypsum crystals. Crystals of this kind were referred to in the original description as "hexagonal plates with unsymmetrical extinction." Some of the various combinations of terminal faces are shown in Fig. 2 *a, b, c, d*. Other crystals were flattened on (010) and showed at

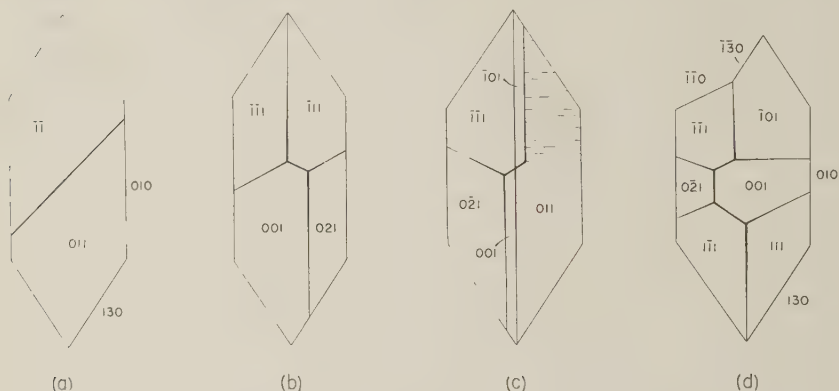


FIG. 2. Variable terminations on crystals. (*a*), (*b*), and (*c*) untwinned. (*d*) twinned on 021, as shown by *x*-ray data.

least some of the faces of the (130) prism, but with no terminal faces. The majority of the single crystals, although showing one or more well-developed faces, presented no obvious clue as to their orientation or the identity of the faces.

TWINNING

Twining on (100) in gypsum gives the familiar "swallow tail" effect. The coesite crystals twinned on (100) showed no such re-entrant angle. The developed end of the twins usually showed a more complex development than did untwinned crystals. But since in the latter the faces (001) (011) and (0 $\bar{1}$ 1) are symmetrical in position with ($\bar{1}$ 01), ($\bar{1}$ 11) and ($\bar{1}\bar{1}$ 1), respectively, there is no morphological evidence that twinning is present. All faces on a twinned crystal can be indexed as if it were a single crystal.

Excellent Weissenberg photographs of both twinned and untwinned crystals, with rotation about the *c* axis, were obtained. If only twinned crystals had been available, a very puzzling situation would have resulted. There is no doubling of spots, as is common with twinned crystals. Since every plane in one twin portion is exactly parallel to a different plane in the other, all reflections can be indexed as from a single crystal. The zero level photographs give no evidence of twinning, for the 0-level

symmetry is C_{21} with $hk0$ symmetrical to $h\bar{k}0$ across 010, and $hk0$ symmetrical to $\bar{h}k0$ across 100 (Fig. 3*b*). The first level films, however, are quite distinctive; $hk1 = h\bar{k}1$ across 010, but $hk1 \neq \bar{h}k1$ across 100. The monoclinic shift between the 0-level and the 1-level is exactly one half of the a^* spacing (Fig. 3*a*). The 1-level reciprocal lattice of an untwinned crystal is shown in Fig. 3*c*. There is a single plane of symmetry perpendicular to the b axis. Both $hk1$ with $h+k$ odd and $h01$ are missing, because of the C lattice and the c glide. On twinned crystals, every permissible reflection is repeated across the b - c plane and falls exactly on a

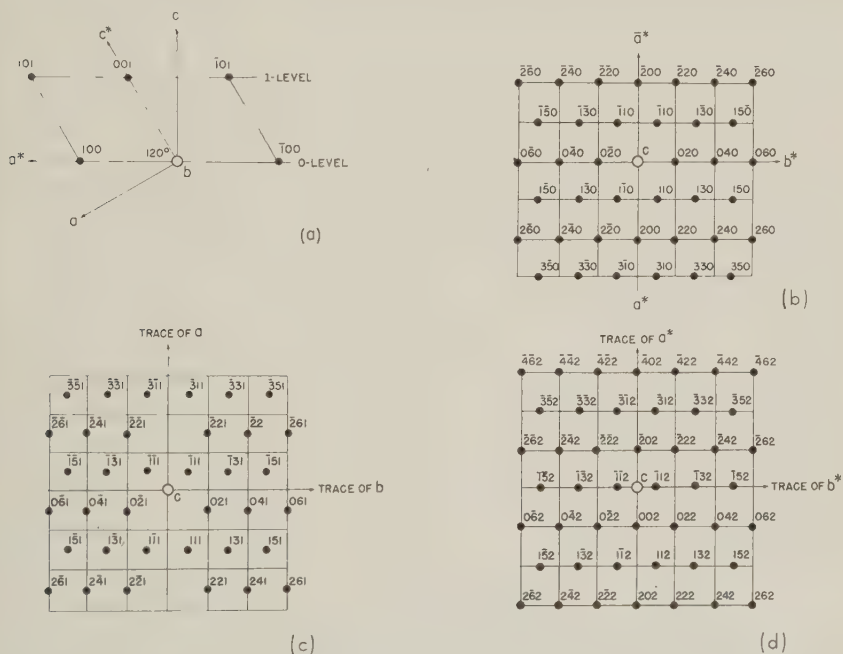


FIG. 3. (a) Monoclinic shift for 1-level reciprocal lattice is exactly $1/2 a_0^*$ spacing. (b), (c) and (d) 0-1-2-levels of reciprocal lattice with rotation about the c axis.

lattice position, but in every case it is a forbidden position, with $h+k$ odd. This is perfectly obvious when untwinned crystals are also found, but if only twinned crystals were available, the situation could easily be misinterpreted.

The second level photograph resembles that of the zero-level, with apparent C_{21} symmetry, resulting from the doubled monoclinic shift (Fig. 3*d*). Every possible reflection with a given value of h has a twinned reflection in a legitimate position, corresponding to $-(h+z)$. Thus 002 is symmetrical to $\bar{2}02$, 112 to $\bar{3}12$, etc. This is not merely an approximate

because these positions may also correspond to reflections from the other portion. Various intensity differences are also noted, because many of the reflections from the twin crystal may be dual.

The most striking evidence of the 021 twinning is found in the 0-level, b axis rotation films. The Weissenberg photograph of an untwinned crystal shows three central lattice lines 60° apart, which are 001 (c^*), $h00$ (a^*) and $h0\bar{h}$. The corresponding Weissenberg of a twinned crystal shows superimposed on this the equivalent of a rotation about the c^* direction, with its b^* central lattice line coinciding with c^* from the other. This relationship is shown in the reciprocal lattice diagrams in Fig. 4. It will be noticed that the twinned crystal gives a larger number of reflections than the untwinned crystal. If they are all indexed as $h0l$ reflections (i.e. b axis rotation) half of the reflections do not agree with the extinctions for the c glide— $h0l$ absent for l odd as shown in Fig. 4c.

Later another crystal was found which did show morphological evidence of 021 twinning. This had a 90° re-entrant angle. Since the 021 plane is at 45° to both b^* and c^* , (010) in one part should be perpendicular to (010) in the other. The common edge of the re-entrant angle is parallel to the a axis. A zero level Weissenberg taken about this common a axis should give a composite photograph, with b^* and c^* (90° apart) from one part coinciding with c^* and b^* of the other. This proved to be the case. There is no doubling of spots, for reflections from both parts coincide. The photograph appears like that of a tetragonal crystal, with symmetry C_{4l} , which is quite different from the zero level, a axis rotation, of an untwinned crystal, where the symmetry is C_{2l} .

This crystal has numerous tiny faces, and other minor re-entrant angles, but many of the reflections were poor, and only five faces could be identified, in addition to the two 010 faces 90° apart. In contrast to the poor morphological data, the Weissenberg photographs were excellent.

One interesting consequence of the 90° re-entrant angle is that when rotated about the a axis on the vertical circle of the goniometer, not only did the reflections from the two 010 planes occur 90° apart, but a continuous weaker signal persisted during the interval between. This is a modification of the well known phenomenon that a beam of light in a plane normal to two mirrors at 90° to each other will be reflected back parallel to itself at any angle of incidence.

UNIT CELL CONTENTS

One puzzling situation occurs with respect to the value obtained for the unit cell contents. Using the cell dimensions as determined from Weissenberg photographs, and a density of 3.01 as determined by the

Norton Company and checked by the writer, the number of formula weights in the unit cell is about 17. Because of the pseudohexagonal character of the monoclinic cell, a value of 18 had been anticipated. However, the space groups Cc and $C2/c$ provide equivalent positions of 4 and 8, respectively, which would require a value of 16.

This discrepancy seems to be too large to be attributed to errors in determining either cell dimensions or density. Chemical tests at the Norton Company included complete volatilization on heating with ammonium bifluoride, and transformation, without change in weight, into silica glass and cristobalite when heated in platinum at 1700°C . These would indicate the new substance is a compound of nothing but silicon and oxygen. A quantitative chemical analysis would be very desirable, to find out if there is any deviation from a strict stoichiometric composition.

ACKNOWLEDGMENTS

The author is grateful for the assistance of Dr. R. B. Roof, Jr., who took some of the x-ray photographs, and to the Office of Naval Research for financial assistance.

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STUDIES IN THE MICA GROUP; POLYMORPHISM AMONG THE HIGH-SILICA SERICITES

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ABSTRACT

X-ray studies on the high-silica sericites indicate that alurgite crystallizes as the *3T* and *2M* polymorphs, that mariposite crystallizes as the *2M* and *1M* polymorphs, and that material called phengite (including sericite) has crystallized as *3T*, *2M* and *1M* polymorphs. The *3T* and *2M* polymorphs have been found intimately associated and have in some specimens formed within the same mica sheet. The precise chemical nature of the individual types is obscure, inasmuch as most of the available analyses have been obtained on samples of mixed structural types. Micas of these types with $2V$ moderate have the *2M* structure; if $2V=0$ -small, the structure is *3T* for well developed crystals of phengites and alurgites and *1M* for poorly-developed crystals of high-silica sericites and mariposite. Neither chemical variation nor environmental control explain the polymorphism.

INTRODUCTION

Schaller (1950), in interpreting the chemical composition of the high-silica sericites, places them in the muscovite-leucophyllite series and demonstrates that they also contain important amounts of a divalent element, usually magnesium. Varieties placed by Schaller (1950) in this series include phengite, mariposite and alurgite. Other investigators including Whitmore, Berry and Hawley (1946), Hutton (1940) and Webb (1939) also have discussed the relationships of these micas to each other and to other members of the mica family. However, adequate information on the structural properties of these minerals has not been available. Hendricks and Jefferson (1939) note that uniaxial alurgite from St. Marcel, Italy, has crystallized as the 3-layer rhombohedral enantiomorphic hemihedral† polymorph, whereas the so-called alurgite from Cajon Pass, California (Webb, 1939) has the common 2-layer monoclinic (*2M*) muscovite structure. Whitmore, et al. (1946), in their work on the chrome micas, note that mariposite conforms chemically with phengite, which agrees closely with Schaller (1950), and they regard it merely as a chromiferous variety of phengite. However, they had no samples of mariposite suitable for x-ray analysis and state that none are recorded

* Contribution from the Department of Mineralogy, University of Michigan, No. 189.

† This polymorph has been referred to as rhombohedral, hexagonal and trigonal by various authors. The nomenclature of Smith and Yoder (1954), in which this polymorph is designated as *3T* (Trigonal), has been adopted and will be used in this paper.

by other investigators. Micas of this type commonly have been reported to exist as two phases, a biaxial and a uniaxial or nearly uniaxial phase, which may be intergrown in the same sheet.

In connection with natural mica studies carried on in the Mineralogical Laboratory under Project M978 of the University of Michigan, Engineering Research Institute for the U. S. Army Signal Corp (Heinrich, et al. 1953), and continued subsequently also by the junior author at the Ohio State University, we have obtained a number of high-silica muscovites suitable for x -ray investigation. Their study reveals that polymorphism is common in high-silica sericites. The Weissenberg method was used wherever feasible, but the flakes of mariposite, of the two alurgites of Meixner (1939), and of the sericites from Amelia, Va., described by Glass (1935) were too minute for Weissenberg techniques, and powder methods were employed. Copper radiation was used throughout.

We wish to thank D. W. Levandowski and C. H. Hewitt for assistance in various details of the investigation and Dr. S. Benedict Levin, Administrator of Project M978 for continuous interest and support. Professor Duncan McConnell has critically read the manuscript. Grateful thanks is given to the following for specimens used: Dr. J. M. Axelrod, Professor C. Frondel, Professor J. Jakob, Dr. H. Meixner, Professor J. Murdoch, Professor A. Pabst, Professor G. Pagliani, Professor R. Parker and Dr. G. Switzer. Dr. H. Yoder kindly aided by supplying information on the identification and differentiation of the *1M* and *1Md* polymorphs.

ALURGITE

Alurgite, St. Marcel, Italy

Both uniaxial and biaxial alurgites from St. Marcel, Italy, the type locality, were studied by means of the Weissenberg method. Some of the flakes contained both uniaxial and biaxial sections. The uniaxial sections have crystallized as the 3-layer trigonal (*3T*) polymorph and the biaxial parts as the common 2-layer monoclinic (*2M*) muscovite polymorph. Penfield (1893) noted that *2E* was as much as 57° ; Larsen and Berman (1934, p. 165) report alurgite, presumably from the same locality, with *2E* as much as 98° . The Penfield (1893) analysis, the only analysis of unquestioned alurgite, apparently was made on material of both uniaxial and biaxial character. Penfield (1893, p. 289) states:

"The largest cleavage plates that have been observed are about 15 mm. in diameter. When examined in convergent polarized light some show a uniaxial others a biaxial interference figure, the double refraction being rather strong and negative. . . . The uniaxial character is undoubtedly the result of twinning, for plates can be found, which in some parts are uniaxial, in others biaxial, and where the plane of the optical axes is in two dif-

ferent positions. Some, moreover, give a confused interference figure, as would be expected from two or more biaxial plates, placed one above the other in twin position. There is no difference in specific gravity between the uniaxial and biaxial plates, they are identical in behavior before the blowpipe and there is every reason for believing that they are the same chemical substance."

It appears possible to simulate a uniaxial interference figure by systematically stacking thin muscovite sheets (Reusch, 1869), but it is structurally impossible to arrange the biaxial portions which have crystallized with the $2M$ structure in any way so that the $3T$ structure results.

Although Penfield (1893) states that alurgite is monoclinic, he notes (p. 289):

"When treated with a mixture of strong hydrofluoric and sulphuric acids the biaxial plates show monosymmetric etching figures while those of the uniaxial plates are triangular or hexagonal, similar to those of muscovite and biotite, described by H. Baumhauer."

The $3T$ structure on St. Marcel alurgite with $2V=0^\circ$ was first established by Hendricks and Jefferson (1939).

Alurgite, East Tyrol, Austria

Meixner (1939) reports alurgites from several localities in East Tyrol, Austria. He confirms the presence of uniaxial and biaxial phases in the St. Marcel mica and states that the red mica from Matrei, East Tyrol, has (p. 697), "Genau die gleichen Eigenschaften. . . ."

Three specimens of alurgite from this locality were obtained from the Museum of Natural History of Vienna. Our examinations show:

Vienna Number	General Appearance	Optical Characteristics	Structure
J2407	Very minute rose flakes	$2V$ -ca. 35°	$2M$ muscovite (Weissenberg method)
G5930	Cryptocrystalline, deep red. Associated with Mn-oxides	$2V$ not determinable	$2M$ muscovite (powder method)
G5931	Cryptocrystalline, deep red	$2V$ not determinable	$2M$ muscovite (powder method)

Since chemical analyses of material from this locality are not available, the mineral cannot be classed as alurgite with certainty. The existence of two optical phases whose presence is intimated by Meixner (1939) (see above) was not substantiated.

Alurgite, India

Fermor (1909), during a systematic study of the manganese deposits of India, reported four occurrences of red and pink mica, in various associations, which he provisionally regarded as alurgite. A small specimen labeled "Alurgite, Ikabis State, Central India" was received from the Harvard Mineralogical Museum. It bears a general color resemblance to alurgite from St. Marcel; the fragment we have received is biaxial with a large 2V. Weissenberg photographs indicate the $2M$ muscovite structure. This material can still be regarded as alurgite only provisionally, as no chemical analysis is known.

"Alurgite," Cajon Pass, California

The type material of Webb (1939) was reexamined by us by the Weissenberg method and the results are identical with those of Hendricks and Jefferson (1939). This mica is not an alurgite chemically, as has been pointed out by Schaller (1950, also in Webb, 1939) because its silica content is that of a normal muscovite. Since its structure is that of the common $2M$ muscovite, it must be classed merely as a ferrian muscovite. Dr. Webb (personal communication) states that he is no longer convinced that his material is true alurgite.

"Alurgite," Ultevis, Sweden

The "alurgite" described by Ödman (1950) contains only 43.67 per cent SiO_2 and 4.36 Fe_2O_3 and is chemically, therefore, a ferrian muscovite and not "alurgite." Weissenberg photographs of flakes of this mica show that it has the common $2M$ muscovite structure.

MARIPOSITE

No mariposite suitable for single-crystal work could be obtained and the powder method was therefore used for structure identification. Two specimens of fine grained mariposite, one from Carson Hill, Calaveras County, California, and the other from San Francisquito Canyon, Los Angeles County, California, the latter described by Murdoch and Webb (1938), have been studied and found to have the $2M$ muscovite structure. Unfortunately, the Carson Hill material is so fine grained and has such poor crystal development that it is impossible to determine the optical properties with certainty. In the case of the San Francisquito material, Murdoch and Webb (1938) state that the mariposite is found in flakes 10-12 mm. in diameter, but these "flakes" are actually aggregates of fine grained material. A few small areas of several of these "flakes" are relatively coarsely crystalline, and from these biaxial interference figures were obtained. 2V was estimated to be as large as 35° . Since no analysis

for SiO_2 was made, this mica could be a chromian muscovite (fuchite with normal SiO_2 , rather than a chromian phengite (mariposite) with high SiO_2).

TABLE 1. X-RAY POWDER DATA ON MARIPOSITES.
(WITH FILTERED Cu RADIATION)

<i>1M</i> polymorph				<i>2M</i> polymorph			
Mother Lode fault zone Mariposa County, California				Carson Hill, Calaveras County, California			
$d(\text{\AA})$	<i>I</i>	$d(\text{\AA})$	<i>I</i>	$d(\text{\AA})$	<i>I</i>	$d(\text{\AA})$	<i>I</i>
10.0	S	2.13	Wd	10.0	S	2.48	MW
4.99	M	2.00	Md	4.99	M	2.39	M
4.48	S	1.72	VW	4.49	S	2.25	W
3.67	M	1.66	Wd	4.32	VW	2.20	W
3.35	S	1.51	S	4.11	VW	2.13	M
3.08	M	1.38	VW	3.88	M	1.99	S
2.84	VVW	1.35	W	3.73	M	1.72	VVW
2.57	S	1.30	W	3.49	M	1.65	M
2.39	M	1.25	W	3.33	S	1.60	VVW
2.26	W			3.20	M	1.56	VVW
				2.99	M	1.50	MS
				2.86	M	1.42	VVW
				2.78	MW	1.35	MW
				2.57	S	1.34	W
						1.30	MW
						1.25	W

Specimens of the mariposite with small 2V described by Knopf (1929) from the Mother Lode area of California as well as the mariposite with $2V < 10^\circ$ from Hoggar, Algeria, described by Sandréa (1950) could not be obtained. However, a specimen from the Rawhide Mine, California (Harvard Museum number 86911) noted by Whitmore, et al. (1946, p. 14) to have a 2V of 12° was secured. Powder x-ray photographs of this material indicate the 1-layer monoclinic (*1M*) mica polymorph.

Another specimen of mariposite received from Professor A. Pabst has also been found to have the *1M* mica structure. This previously undescribed specimen was collected from the "Mother Lode fault zone north of State Highway 140, northeast corner of Indian Gulch quadrangle, Mariposa County, California." It is typical of all mariposite specimens seen and is intimately associated with quartz. 2V could be determined on only one flake and was noted to be approximately 10° . Although careful selection of other mariposite flakes under a microscope had usually yielded pure material (no extraneous x-ray powder lines), the

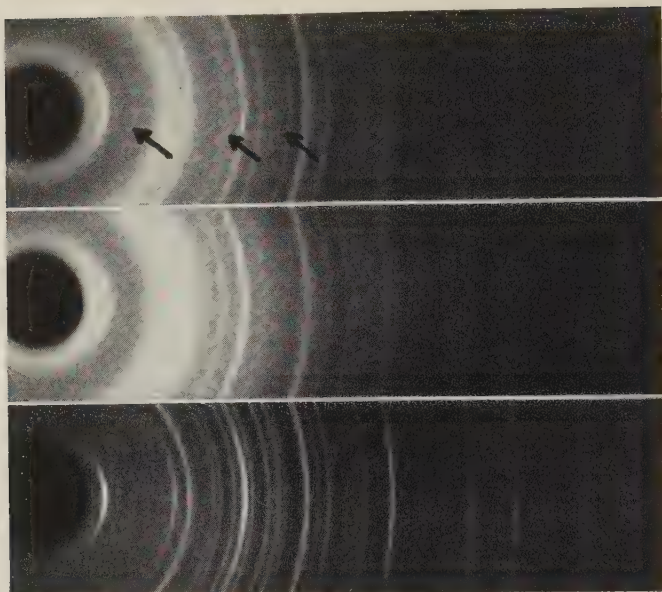


FIG. 1. *Top*: Mariposite from Mother Lode fault zone, Indian Gulch quadrangle, Mariposa County, California, showing $1M$ structure contaminated with lines of a kaolinite type mineral (arrows). *Middle*: Same material as above heated for 3/4 hour at 575° C. in air showing diffraction lines only of the $1M$ mica polymorph. *Bottom*: Mariposite, Los Angeles County, California described by Murdoch and Webb (1938) showing $2M$ structure. This pattern is essentially identical with that of $2M$ mariposite from Carson Hill, Calaveras County, California (Table 1).

(All photographs with filtered copper radiation.)

Indian Gulch mariposite showed contamination by a kaolinite-type mineral, with characteristic diffraction lines at 7.1, 3.55, etc. After the specimen was heated to 575° C. for 3/4 of an hour, the lines attributed to the kaolinitic mineral disappeared. Figure 1 illustrates the powder patterns of the $1M$ structure obtained from this mariposite both before (top) and after heating (middle). Table 1 lists the interplanar spacing of a $1M$ mariposite.

PHENGITE

Phengite, Fontane, Germanasca Valley, Italy

The phengite analyzed and described by Pagliani (1937) is reported to have a $2V$ of about 11° . The $2V$ of the type material we received is larger than 11° , ranging generally from 18° to 35° (estimated). Weissenberg photographs of sections with $2V$ near 35° show the $2M$ muscovite structure, but photographs of the sections with the smaller $2V$ have patterns of the $2M$ form combined with what appears to be the $3T$ poly-

morph. It is probable that patterns of the phengite with $2V=11^\circ$ might be those of the $3T$ polymorph alone.

Specimens of a mica called muscovite by Jakob (1929A, his number 43) have been studied. This mica, from Passo di Ganano, Soazza, Val Mesocco, is uniaxial, and Weissenberg photographs show that it has crystallized as the $3T$ structure. It is a high-silica muscovite ($\text{SiO}_2=49.01$ per cent) and has the required, relatively large, content of a divalent element, $\text{MgO}=3.91$ per cent. This mica probably was called muscovite by Jakob (1929A), rather than phengite, because of its occurrence and paragenesis, for the term phengite apparently has been used by some investigators for very fine grained high-silica muscovites of secondary origin. Although this mica is predominantly uniaxial, several small basal areas in a few flakes show birefringence and have a moderate $2V$. One such isolated biaxial part proved to have the $2M$ muscovite structure.

Phengites with the $2M$ muscovite structure

Jakob has analyzed five other high-silica muscovites all of which we have examined and found to have the normal $2M$ muscovite structure. Data on these micas are as follows:

Reference	Name	SiO_2	MgO	FeO	Fe_2O_3
Jakob (1925) No. 18	muscovite	50.79	2.80	1.34	2.94
Jakob (1929A) No. 44	phengite	50.64	4.15	1.01	2.97
Jakob (1929A) No. 45	sericite	48.80	5.74	0.00	5.86
Jakob (1929A) No. 46	sericite	50.20	3.82	0.00	9.62
Jakob (1929B) No. 54	muscovite	50.04	3.64	0.85	2.44

Nos. 18 and 54 have normal $2V$ s; the others are too fine grained for $2V$ determination.

Phengite from Adula Mountains, Switzerland

The mica from Mt. Mucrone, Switzerland, described by Kunitz (1924) is uniaxial and is called phengite ($\text{SiO}_2=50.45$ per cent) by him. Specimens of this material could not be secured for x -ray studies.

Axelrod and Grimaldi (1949, p. 560) note, "Carl Schmidt found, in a gneiss from the Adula Mountains, Switzerland, a green pleochroic muscovite that was uniaxial. It became biaxial on heating and on cooling became uniaxial again."

Analyses of what appears to be similar uniaxial material, and also of an associated biaxial mica ($2E=52^\circ$) from the Adula Mountains, also collected by Schmidt, have been reported by Wülfing (1886). Analyses of both types indicate slightly high silica (47.69 and 47.72 per cent), high MgO (2.72 and 2.30 per cent) and high total iron (4.90 and 8.31 per

cent), values which are essentially characteristic of phengite. The most striking difference in the two analyses is the higher ferrous iron content of the biaxial part, i.e. 6.55 per cent FeO as compared with 3.88 per cent for the uniaxial material.

A sample supposedly of Wülfing's (1886) uniaxial phengite was obtained from the Museum of Natural History of Vienna (No. G3399). Optical examination of the sample reveals the presence of two phases: a uniaxial type and a normal biaxial muscovite, which are otherwise markedly similar. Weissenberg photographs of the uniaxial variety show it to possess the $3T$ structure, whereas the mica with the normal $2V$ has crystallized as the $2M$ muscovite type. In view of this admixture of the two varieties in material supposed to be homogeneous, it is doubtful that the chemical differences reported by Wülfing (1886) are significant.

Sericites from Amelia, Virginia

Glass (1935) has described five sericites from Amelia, Virginia. Powders of the analyzed material were secured from the U. S. Geological Survey, and powder x-ray patterns were obtained.

Varieties 1 and 2 have slightly high silica contents (48.06 and 47.22 per cent) as well as MgO contents (1.39 and 1.25 per cent) and probably should be considered related to the above mentioned phengites. $2V$ is reported from $70-80^\circ$ for variety 1 and $70-75^\circ$ for variety 2. X-ray studies on these varieties indicate the 1-layer monoclinic mica structure. However the (112) and $(11\bar{2})$ reflections, which correspond with approximately $d=3.08 \text{ \AA}$ and 3.67 \AA respectively, are of low intensity. On the basis of the experiences of Yoder and Eugster (1954, p. 173) and Levinson (1955) the low intensity of these reflections is probably caused by a random stacking of the mica layers. Yoder and Eugster (1954) show several degrees of ordering between a completely disordered ($1Md$) and an ordered one-layer ($1M$) phlogopite. The degree of ordering of these sericites is not easily determined and they may approach closely the $1Md$ type.

Varieties 3 and 4 have silica contents that are essentially normal (46.81 and 46.80 per cent), as are their MgO contents (0.62 and 0.56 per cent). $2V$ is reported as $30-40^\circ$ and variable for both types. X-ray powder patterns of both varieties are identical. Although they contain characteristic mica lines it was not possible to determine the polymorph with certainty.

Variety 5 is a true phengite or high-silica sericite with 49.16 per cent SiO_2 and comparable high MgO (2.22 per cent). Glass (1935) reports $2V$ for this specimen as $0-3^\circ$. An x-ray powder pattern of this mica shows that it has crystallized with the $2M$ structure. The optic angle of this mica, as well as those of the other micas could not be checked because of the extremely fine grained nature of the powdered sample.

DISCUSSION

It has generally been assumed from the work of Hendricks and Jefferson (1939) that muscovite crystallizes with essentially one structure, the *2M*. However, these muscovites appear to be predominantly, if not entirely, of pegmatitic origin. The mica from Sultan Basin, Washington, described by Axelrod and Grimaldi (1949), which is now known to be *3T* (Smith and Yoder (1954)), and has been considered anomalous by some investigators, is not of pegmatitic origin. The results of our investigation further indicate that the *2M* polymorph is not unique for muscovite-type micas and especially for the high-silica types of hydrothermal and metamorphic origins. Similar results, in which the *3T*, *2M*, *1M* and *1Md* polymorph have been found, are described by Levinson (1955) among the hydrous micas. Also Heinrich and Levinson (1955) have determined the structures of some roscoelites and a barium-muscovite to be *1M*. Clearly the *2M* structure can not be considered representative or unique for muscovite-type micas as a whole.

The data presented in this paper show some definite relationships between crystal structure, *2V* and crystal development. In the case of the phengites and alurgites that are sufficiently well developed for Weissenberg study, the following relationships have been observed: if *2V* is 0° or small (less than approximately 15°), the structure is *3T*; if the mica is distinctly biaxial with a moderate or large *2V*, the structure is *2M*. In the case of the very fine grained, poorly developed, high-silica sericites and mariposite, which required study by the powder method, the following characteristics have been observed: if *2V* is moderate or large, the structure is *2M*; if *2V* is 0° or small, the *1M* (or *1Md*) structure obtains. The *2V* of the high-silica sericites described by Glass (1935), which are not in accord with the above generalizations, have not been redetermined by us, and therefore, are not considered in these conclusions. Therefore the high-silica muscovites with small *2V* are worthy of further study, because they are the type in which to date the *1M* and *3T* polymorphs have been found. In addition to the examples discussed, several others of this type have been reported, specimens of which we have been unable to obtain. These are briefly noted below.

Scheerer (1862, p. 63) described two uniaxial micas from a gneiss near Freiberg, Germany, which are high in silica and are considered to be phengite.

Buryanova (1940) reports a yellowish-green mica with $2V = 8^\circ$ from a granitic pegmatite of the Korosten pluton in Volhynia. It is associated with albitized orthoclase, lamellar albite, fluorite and a markedly biaxial mica.

Clark and Hunt (1915) concluded that the mica in a dolomitic marble

TABLE 2. DATA ON ALURGITES, MARIPOSITES AND PHENGITES

Name	Locality	Optic Angle	Structure	Reference	Occurrence and Origin
Alurgite	St. Marcel, Italy	2V=0°	3T	Penfield (1893)	Metamorphic manganese deposits
Alurgite	St. Marcel, Italy	2V=ca. 35°	2M	Penfield (1893)	Metamorphic manganese deposits
Alurgite	East Tyrol, Austria	2V=ca. 35°	2M	Meixner (1939)	Metamorphic manganese deposits
Alurgite	East Tyrol, Austria	2V=?	2M	Meixner (1939)	Metamorphic manganese deposits
Mariposite	Calaveras Co., Calif.	2V=?	2M	This paper	{Hydrothermal; associated with ankerite, quartz, sulfides and gold veins.
Mariposite	Rawhide Mine, Calif.	2V=12°*	1M	Whitmore, et al. (1946)	
Mariposite	Mariposa Co., Calif.	2V=ca. 10°	1M	From A. Pabst	
Mariposite	Los Angeles Co., Calif.	2V=moderate	2M	Murdoch and Webb (1938)	In talc schist
Phengite	Fontane, Italy	2V=ca. 35°	2M	Pagliani (1937)	Mica schist overlying talc lens
Phengite	Fontane, Italy	2V=ca. 18°	2M+3T?	Pagliani (1937)	Mica schist overlying talc lens
Phengite	Adula Mts., Switz.	2V=0°	3T	Wülfing (1886)	Gneiss
Phengite	Adula Mts., Switz.	2V=moderate	2M	Wülfing (1886)	Gneiss
Phengite	Val Mesocco, Switz.	2V=0°	3T	Jakob (1929A)	Alpine cleft vein in eclogite
Phengite	Val Mesocco, Switz.	2V=moderate	2M	Jakob (1929A)	Alpine cleft vein in eclogite
Sericite	Amelia, Virginia	2V=70-80°*	1M	Glass (1935) var. 1	{Secondary, alteration of feldspars and topaz
Sericite	Amelia, Virginia	2V=70-75°*	1M	Glass (1935) var. 2	
Sericite	Amelia, Virginia	2V=0-3°*	2M	Glass (1935) var. 5	

W=Structure determined by Weissenberg method.

P=Structure determined by powder method.

* = Indicates 2V obtained from literature and not redetermined.

2V=0° may indicate a very small 2V.

Moderate=distinctly biaxial with 2V approximately 30-40°.

from Cockeysville, Maryland, was a muscovite, even though it has the optical properties of a phlogopite. Their conclusion was based on a partial analysis of the rock which showed a discrepancy in the $\text{Al}_2\text{O}_3:\text{SiO}_2$ ratio for phlogopite. A specimen of this mica has been examined by the Weissenberg method and the structure determined to be *1M* with intensities identical with *1M* phlogopites. It is, therefore, a phlogopite and not a muscovite with a small 2V.

Shibata (1952*A*, p. 135) notes, with respect to a mica from the Bunsen Mine, Korea: "White mica associated with pink lepidolite is uniaxial negative under the microscope and is considered as phengite." An analysis of this material is also presented (Shibata 1952*B*, p. 150). Shibata (1952*B*) also describes a "lithium phengite" from the Uruchin Mine, Korea and states (p. 153): "... is optically uniaxial and has high contents of iron and magnesium. These characteristics coincides (sic) with those of phengite and this variety is to be called for 'Li-phengite' (sic) by its high content of lithium."

The cause of the polymorphic variations is not known. Several possibilities have been considered, but the results are inconclusive. For example, no systematic differences in composition are known to distinguish the several structural types. Actually there is no certainty as to whether the few available analyses were carried out on completely uniaxial (*3T* or *1M*) or biaxial (*2M*) material, except possibly those of Wülfing (1886). From the small-scale nature of the optical variation, material of both types may have been involved in each analysis. The phengite of Pagliani (1937) is a good example; the literature indicates that the analysis was performed on material with a 2V of about 11° , whereas the material sent by Professor Pagliani has a predominant biaxial phase. It does not seem likely, however, that the control of the polymorphism can be ascribed entirely to compositional variations. High-silica sericites of apparently the same composition may or may not crystallize as several polymorphs. If the high silica content exercises any control on the structure, it seems to be a permissive rather than a requisite control.

The environmental factors are even more difficult to evaluate. Table 2 lists most of the high-silica sericites studied together with 2V, structure, their mode of occurrence, and available information regarding their origin. Although the data are incomplete, it is striking that none of these micas formed by crystallization from a granitic or pegmatitic magma. They are either of hydrothermal origin or occur in metamorphic rocks, in which their origin is unspecified. These relations suggest that, if the polymorphism is controlled in any way by or related in any manner to the high silica or associated chemical content, an unknown physical factor, furnished by a hydrothermal or metamorphic environment, also

must be active in crystallization. Any such postulated environmental control must be exceedingly delicate in order to account for the small-scale intergrowths of the two polymorphs in the same sheet, as in the case of alurgite. In order to solve this problem, more muscovites must be studied, and new analyses made on material of uniaxial character must be compared to analyses of material that is entirely biaxial.

NOTE ADDED IN PRESS:

M. Nakahira (*Acta Crystallographica*, **7**, p. 684, 1954) has observed "... a two-layered (muscovite-type) and a three-layered (pseudo-trigonal) structure, or an intermediate type of these two" in sericites from the Unnan Mine, Shimane Prefecture, Japan. No optical or geologic data are given in his abstract.

S. Kilpady and A. S. Dave (*Proc. Indian Acad. Sci.*, **39**, pp. 53-63, 1954) have described what they believe to be an alurgite from a pegmatite at the Sitasonggi Mine, Bhandara District, India. Because of its normal SiO_2 content (45.6 per cent) and high Fe_2O_3 content (5.8 per cent) this mica should be called a ferrian muscovite. We have determined the polymorph of a specimen of this crimson mica received from Dr. Kilpady to be *2M* and thus it is structurally a normal muscovite.

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THE ACTION OF HOT WATER ON SOME FELDSPARS

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ABSTRACT

Hot water was passed over the feldspars contained in closed bombs, the total amount of solution weighed and analyzed, and the material remaining in the bomb studied with α -rays and the petrographic microscope. At 350° C., 5000 psi, the solution obtained from orthoclase and from albite contained over 90% of the dissolved material in the feldspar ratio. At lower temperatures and pressures, 200° C. and 2000 psi, and 100° and 40 psi, albite was decomposed in greater proportion. At 350° and 2000 psi a large amount of analcime was found in the albite experiment, but none at the lower temperatures.

There have been many studies of the reaction between water and feldspars. Some of these were in the earliest periods of hydrothermal experimentation, when pressures were not controlled and not known, and the emphasis was chiefly on the synthesis of the feldspars. Other experiments dealt with the decomposition of feldspars by acid, alkaline, or salt solutions. These experiments have been critically summarized by Morey and Ingerson (1937). Bowen and Tuttle (1950) studied the system $\text{H}_2\text{O}-\text{NaAlSi}_3\text{O}_8-\text{KAlSi}_3\text{O}_8$ at pressures up to 2000 bars and temperatures up to 800° C. However, there have been few studies of the effect of water alone below its critical temperature—just hot water. Norton (1937) studied the alteration of orthoclase, anorthite, and albite by liquid water containing from 1 to 23% carbon dioxide at temperatures from 225° to 350° C. The experimental arrangement was such that the finely powdered feldspar was subjected to a continuous extraction by freshly condensed liquid for 10 to 33 days. Albite was but slightly altered, with possible formation of paragonite; orthoclase was converted to sericite.

The apparatus we used (Fig. 1) was similar to that used by Morey and Hesselgesser (1951) in their study of the solubility of some minerals in superheated steam. Distilled water is pumped into a pressure line, in which there are a pressure gauge, pressure cylinder, ballast cylinder, filter, and a bomb made from 303 stainless steel. The connecting high-pressure tubing also is of stainless steel. The pressure gauge is a calibrated Bourdon gauge; the pressure regulator a Baldwin fluid pressure cell, the sensitive elements of which are two Baldwin strain gauges used in conjunction with a special Brown electronic potentiometer. The ballast cylinder has a volume of 2240 ml., and the leads to it are so arranged that the flow may be in either direction. In the pressure line, just before the bomb, is a small cylinder which contains amberlite IR-120 (H) cation exchange resin followed by a porous stainless steel filter with a mean pore

opening of 20 microns. This is to remove any contaminant, especially iron oxide resulting from corrosion in the pump or pressure line. The water passes through the heated bomb, then through a zig-zag cooling coil, to the throttling valve, after which it is collected, weighed, and analyzed. The furnace has two windings, each of which is controlled by a Brown electronic controller, using chromel-alumel thermocouples inserted in wells as indicated. Temperature is measured by platinum-10%

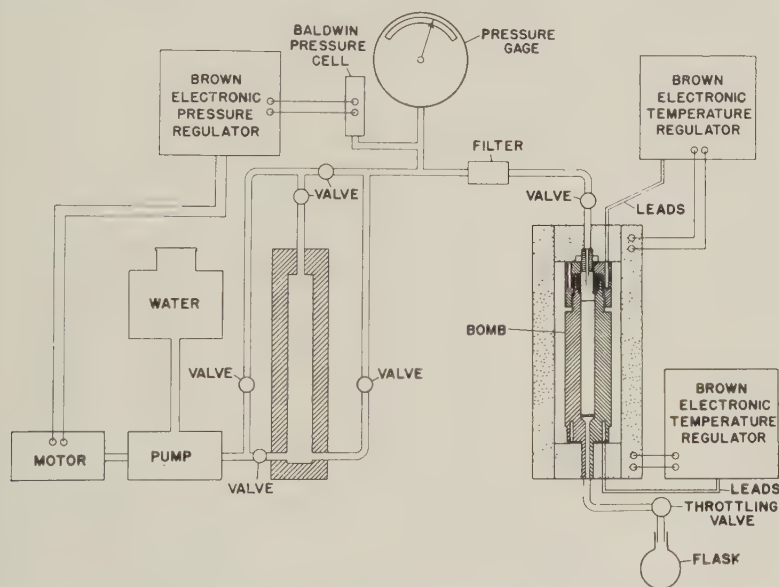


FIG. 1. Diagrammatic outline of pressure apparatus. Distilled water is pumped into the pressure line, which includes a reservoir, a reading gauge, and a regulator to maintain the pressure constant. The solid material is contained in the bomb and heated in the regulated electric furnace. The water is changed to steam, passes over the solid and out of the bomb, constant pressure being maintained on the cooled water until the throttle valve is reached. The condensed water is collected, weighed, and analyzed.

rhodium thermocouples similarly placed in wells in the bomb, and the two temperatures are maintained the same within $\pm 2^\circ \text{C}$.

The first series of runs were made at 350°C ., 5000 psi, using microcline from the Derry mine in Quebec, crushed to pass $1/4''$ mesh, and held on a 20-mesh screen, and the fines were removed by washing. The feldspar rested on a porous stainless steel filter, having a mean pore opening of 20 microns, and was covered with a similar filter. The solution was caught in 3-liter flasks, acidified with HCl , and evaporated to dryness in large porcelain dishes. Analyses were made by standard methods (Hillebrand and Lundell, 1929). The SiO_2 was filtered off after the usual treat-

ment with concentrated HCl, the filtrate again evaporated to dryness, and the precipitate digested overnight with dilute HCl. The combined SiO_2 was ignited to constant weight, evaporated with HF and H_2SO_4 , and the SiO_2 determined by difference. The residue was Al_2O_3 , which was added to the main portion. Al_2O_3 was determined by double precipitation with NH_4OH and ignition to constant weight. The ammonium salts in the filtrate were removed by heating with concentrated HNO_3 , the residue converted to sulfate, and weighed as K_2SO_4 . It was difficult to be sure all the material was removed from the large porcelain dish, but the same dish was used repeatedly without further washing for each determination, so that the total error from this source was small.

This run lasted 103 days. The total weight of solution was 194,432 g., and the total weight of dissolved material 52.1564 g., which is 268 parts per million. This is not a true solubility. None of the results reported here represent a true solubility, but represent rates of reaction under the conditions of the experiment. The amounts of constituent oxides dissolved were: K_2O , 8.9268; Al_2O_3 , 8.6760; SiO_2 , 34.5536. These are in the weight ratio of 1.03:1:3.98, or in the mole ratio of 1.11:1:6.76. If all the Al_2O_3 is calculated to orthoclase, it would give 47.3580 g., or 90.8%. Under the requisite conditions, this presumably could be transported and could crystallize out as orthoclase.

The remainder in solution, after subtracting K_2O , Al_2O_3 , and SiO_2 corresponding to the above amount of orthoclase, is an excess of K_2O and Al_2O_3 . The amounts are: K_2O , 0.9091 g.; SiO_2 , 3.8893. These are in the molecular ratio of 1:6.71.

The residue remaining in the bomb was studied with both the petrographic microscope and x -rays. There was much orthoclase remaining, both as large fragments and as fine powder. The large fragments had a white coating, which proved to be muscovite and boehmite, $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$. The greater part of the fine-grained material in the bomb was boehmite. If $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$ is decomposed and leaves a residue of either muscovite or boehmite, the solution should contain excess $\text{K}_2\text{O}:\text{SiO}_2$ in the ratio of 1:6. The ratio found was 1:6.71. This could be due to analytical error or to formation of an amount of a clay mineral too small to detect with either the microscope or x -ray.

Three separate runs were made with albite. The first of these was at 350°C ., 5000 psi, and lasted 38 days. It was terminated by the exit tube being stopped up with analcime, $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot 2\text{H}_2\text{O}$, and there was some analcime on the filter disc above the albite. The total weight of solution obtained was 78,005 g. The amounts of constituent oxides dissolved were: Na_2O , 2.8358 g.; Al_2O_3 , 4.4307 g.; SiO_2 , 17.5250 g.; a total of 24.7915 g., corresponding to 318 parts per million dissolved material. The dis-

solved material has a weight ratio $\text{Na}_2\text{O}:\text{Al}_2\text{O}_3:\text{SiO}_2$ of 0.64:1:3.96, and a mole ratio of 1.05:1:6.71. The amount of albite corresponding to the amount of dissolved alumina is 22.79 g., or 91.9% of the total solution. The excess Na_2O is 0.1415 g. and excess SiO_2 , 1.8624 g., a mole ratio of $\text{Na}_2\text{O}:\text{SiO}_2$ or 1:13.6.

The material remaining in this bomb was in part a fine powder, in part original grains of albite covered by a thin white coating, and there was well-formed analcime between the upper filter plate and the top of the bomb. The white coating on the albite proved to be largely muscovite, with some paragonite. The Amelia County, Va., albite was from the same lot as that used by Day and Allen (1905), which contained 11.47% Na_2O and 0.20% K_2O . The amount of muscovite which would correspond to all the K_2O corresponding to the known amount of Na_2O which was found in the solution would be 0.41 g. Practically all the K_2O must have been held in the surface as muscovite. This reaction has interesting implications with regard to the common sericitic alteration of plagioclase. We are grateful to our colleague Dr. H. S. Yoder for making an intensive study of the muscovite, which proved to be exceptionally good crystals of a 1*M* muscovite. The fine powder in the bomb was chiefly boehmite, $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$, together with some analcime.

If the albite were completely dissolved as albite, or if it were completely decomposed leaving boehmite, the mole ratio of $\text{Na}_2\text{O}:\text{SiO}_2$ in the solution should be 1:6. The ratio found was 1:13.6. This excess could be caused by the formation of analcime, $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot 2\text{H}_2\text{O}$. The amount of analcime calculated from the 1.8629 g. of excess silica is 6.5 g., which probably is of the right order of magnitude.

A similar run was made with a powdered albite at 200° C. and 2000 psi. In this case the total weight of water collected was 279,438 g. The total amount of material dissolved was 14.6594 g., which is equivalent to 53 parts per million. The total of the analyses gives: Na_2O , 2.1127 g.; Al_2O_3 , 2.0167 g.; SiO_2 , 10.5300 g. This is a weight ratio of $\text{Na}_2\text{O}:\text{Al}_2\text{O}_3:\text{SiO}_2$ of 1.05:1:5.22, or a mole ratio of 1.72:1:8.86. If the alumina is calculated to albite, it gives 10.372 g. albite, or 70.7% of the total amount of dissolved material. The excess of Na_2O is 0.8873 g.; of SiO_2 , 3.2626; which gives a mole ratio of 1:3.8. Examination of the residual material showed no analcime whatever, only residual albite, boehmite, and some kaolinite. The kaolinite lines were strong.

Another run was made with powdered albite at 100° C. and the city water pressure, about 40 pounds. The container in this case was a tube of Airdi steel, which unfortunately was strongly attacked, and the solution carried over a considerable amount of iron oxide. As the solution first came over it was clear and colorless, but on standing it gradually

precipitated red ferric oxide, and it is probable that the iron is originally in solution as ferrous oxide. The city water used in this run was passed through a Barnstead demineralizer cartridge. The weight of the alumina was corrected for the iron oxide content, as determined by fusion with pyrosulfate, solution of the melt, reduction in a Jones reductor, and titration with potassium permanganate. The total weight of water collected was 384,269 g. The total amount of material dissolved was 2.4411, which is equivalent to 6.4 parts per million. The total of the analyses gives: Na_2O , 0.3349 g.; Al_2O_3 , 0.2333 g.; SiO_2 , 1.8729 g. This is a weight ratio of $\text{Na}_2\text{O}:\text{Al}_2\text{O}_3:\text{SiO}_2$ of 1.44:1:8.03, or a mole ratio of 2.35:1:13.57. If all the alumina is calculated to albite it gives 1.2063 g., or 49.4% of the total dissolved material. The excess of Na_2O is 0.1923 g.; of SiO_2 , 1.0437 g., which gives a mole ratio of 1:5.5. In this case also muscovite was found on the surface of the albite grains, and the altered residue consisted of boehmite and kaolinite.

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ANALYSIS OF HAMLEY BORNITE FROM SOUTH AUSTRALIA

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ABSTRACT

The physical and chemical analysis of a bornite from the Hamley Mine, Moonta, South Australia, is given. The composition of the selected sample conforms very closely indeed to that demanded by the formula Cu_5FeS_4 .

The analysis of bornite given in this paper was made at the request of J. W. Greig and H. E. Merwin of this Laboratory, who, after its purity was established, used it in connection with their work on the Cu—Fe—S system. This material was selected for them by W. F. Foshag and bears the U. S. National Museum number R702. It came from the Hamley Mine, Moonta, South Australia.

Preliminary microscopic examination revealed the presence of small amounts of quartz and of a reddish alkali feldspar, and microscopic examination of polished areas showed the presence of a very small amount of a second opaque mineral as minute irregularly shaped particles in the bornite. An adequate sample was coarsely crushed by gentle tamping and the coarse gangue removed by hand-picking. The tamping was continued until all particles passed through a 30 mesh bolting cloth; everything finer than 118 mesh was rejected. Examination with the microscope had shown that this range of particle size was just about right to yield by means of an electromagnet almost complete separation of the bornite and fine-grained gangue. This size was also well adapted for the chemical analysis, especially so since the error introduced by oxidation of finely divided sulfides was avoided.

Several hundred grains of the purified sample were mounted, polished, and examined in polished section. The only opaque substance, other than bornite, found in the grains was a whitish mineral, which a careful count showed was present to the extent of 0.1%. This impurity has not been identified and hence is not accounted for in the analysis given in Table 1. Its amount is, however, too small to significantly affect the results.

X-ray analysis of the selected material by J. V. Smith showed that its pattern was identical with that of bornite (Cu_5FeS_4). Since neither the microscopic examination nor the x-ray analysis proves that this bornite does not contain material in solid solution, or sets a limit to the possible content of such material, the sample was subjected to chemical analysis.

The procedures used in determining the various constituents were essentially those given by Hillebrand, Lundell, Bright, and Hoffman (1953). It should be mentioned, however, that since no method for analyzing bornite is given in this book we feel that it is desirable to give a few salient analytical details. It is, of course, well known that a substance is rarely completely precipitated in a chemical analysis. For this reason we tried to recover as well as possible the amounts that escaped into the filtrates. We found that the sulfur in bornite can be completely oxidized to sulfate, without separation of free sulfur, by the Allen and Bishop method for pyrite (see Hillebrand *et al.*, 1953, p. 712). When the sample was completely decomposed, the oxidizing acids were destroyed in the usual manner with hydrochloric acid. The small amount of residue

TABLE 1. ANALYSES OF HAMLEY BORNITE

	1	2	3	4	5	Average
Cu	63.10 ^a	62.99 ^b		62.92 ^b	62.93 ^b	62.99
Fe	11.07 ^c	11.12 ^c		11.20 ^d	11.16 ^d	11.14
Co						0.05 ^b
Ni						0.01 ^b
S			25.46	25.54	25.44	25.48
Residue ^e	0.18	0.25	0.28	0.23	0.23	0.23
Sum						99.80

^a Weighed as metallic Cu after separating from Fe with H₂S.

^b Weighed as CuCNS and corrected for its solubility.

^c Through KMnO₄ after reduction with H₂S.

^d Weighed as Fe₂O₃.

^e Examined microscopically before ignition and found to consist of quartz and alkali feldspar.

^f Determined on a separate sample.

insoluble in acids was determined by ignition and weighing in the same manner as for silica. When viewed under the microscope before ignition it was found to consist of quartz and a flecked alkali feldspar. Additional brief details of the analytical procedure are given in the footnotes to Table 1. In addition we should like to mention that especial attention was given to the determination of the sulfur content of the bornite. As can be seen in the case of analyses 4 and 5, all three constituents and the residue were determined in the same sample. This is possible because copper and iron can be almost completely separated from SO₄ in boiling solution by a double precipitation with a slight excess of measured amounts of a solution of pure sodium carbonate. The end point is reached when the precipitate turns black. The filtrate is essentially a

solution of sodium sulfate. It is diluted to 500 ml., acidified to the extent of 1.0% HCl and barium sulfate precipitated in boiling solution. It is well known that the weight of barium sulfate is subject to a plus error. The correction is easily applied by the C. E. Waters method (see Hillebrand *et al.*, 1953, p. 721). The SO_4 content is determined for a solution that contained an amount of pure sodium sulfate equivalent to the sodium carbonate used in the precipitation of the copper and iron. The procedure used in making this determination must be the same as for the unknown. The difference between the theoretical and the found values is, of course, the correction.

If we deduct the residue and recalculate the average values we obtain:

	Hamley bornite	$\text{Cu}_5\text{FeS}_4^*$
Cu	63.13	63.31
Fe	11.18	11.13
Co	0.05	
Ni	0.01	
S	25.54	25.56
Sum	99.51	100.00

* Values based on International Atomic Weights of 1951.

It is obvious that the chemical analysis of this bornite selected from the sample obtained from the Hamley Mine in South Australia conforms closely to the accepted formula Cu_5FeS_4 and agrees well with the analyses of the purest bornites given in *Dana's System of Mineralogy* (1944, p. 196). We also wish to state that our evidence agrees with the opinion so well expressed by E. T. Allen in 1916: "Aside, then, from those slight variations in composition which are so common throughout the mineral kingdom, and which are due to foreign admixtures or to solid solution, there is, in my opinion, no satisfactory evidence that natural bornite is variable in composition, or that it is ever of any other composition than that expressed by the formula Cu_5FeS_4 ."

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SOME THERMODYNAMIC RELATIONS AMONG THE URANIUM OXIDES AND THEIR RELATION TO THE OXIDATION STATES OF THE URANIUM ORES OF THE COLORADO PLATEAUS*

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ABSTRACT

Fields of stability of uranium (VI) and uranium (IV) hydroxides and oxides in water solution at 25° C. and one atmosphere pressure have been calculated as functions of Eh and pH. Equilibrium values of the activity of UO_2^{++} ion and of U^{4+} ion also have been calculated and are shown as contours on the stability fields. Thermodynamic relations among the uranium (VI) hydroxides and hydrated oxides indicate that the free energy differences among the various species are small. The data are interpreted to mean that a variety of such uranium (VI) compounds may form and even coexist. Similar studies of the uranium (IV) hydroxide indicate that it is unstable relative to the oxide and may well be expected to change to the oxide at a finite rate. Uranium (V) compounds probably have a transitory existence because of the instability of the UO_3^+ ion; uranium (III) oxides and hydroxides would not be expected to occur naturally because the uranium (III) ion would decompose water. A comparison of the behavior of the vanadium (III) and (IV) hydroxides with uranium (IV) oxide and uranium (VI) hydroxides indicates that vanadium (III) hydroxide should oxidize to the vanadium (IV) hydroxide at a lower potential than that required for the change from uranium (IV) to uranium (VI). A rather highly speculative diagram showing probable fields of stability of many of the major minerals of the Colorado Plateaus is presented, and the suggestion is made that a consistent picture results if it is assumed that the ores, as viewed today, represent the superimposition of a weathering environment on a mineral assemblage that was formed in a primary reducing environment. It is emphasized that such an interpretation is consistent but not necessarily unique.

INTRODUCTION

Prior to about 1950, the uranium-vanadium ores of the Colorado Plateaus presented few problems in the interpretation of the oxidation-reduction conditions of their environment of formation. The oxidation-reduction "sensitive" elements of the major minerals uniformly exhibited the higher valences consistent with moderate to strongly oxidizing environments. During the last several years this consistency has disappeared; with the discovery of large quantities of "blue-black" or "black" ores, a variety of minerals containing the same elements, but in lower valence states, have become of economic importance.

The genetic relation of the "blue-black" ores to the more oxidized, or "carnotite" ores, is not clear, but one definite possibility is that the primary ores were an assemblage of minerals deposited under reducing conditions, and hence with the "sensitive" elements in their lower

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valence states, and that the more oxidized ores have been, at least in part, derived from them by ordinary weathering processes. If so, the primary oxidizing agent was oxygen carried by ground water, and the temperature and pressure of the reactions were close to 25° C. and 1 atmosphere.

The stability relations of many of the minerals involved under such conditions can be calculated. In a previous paper (Garrels, 1953) relations of some of the vanadium oxides were considered. In this report various uranium oxides, hydroxides, and hydrated oxides, for which thermodynamic data are available, are discussed.

This work was done on behalf of the Division of Research of the U. S. Atomic Energy Commission. C. R. Naeser of the Geological Survey was a constant source of information and guidance during the preparation of the manuscript and gave freely of his time in clarifying numerous aspects of the chemistry for the author.

THERMODYNAMIC PROPERTIES OF SOME COMPOUNDS AND IONS OF THE SYSTEM U-O-H₂O

Data on the thermodynamic properties of compounds and ions in the system U-O-H₂O have been assembled (Table 1) from Latimer (1952)

TABLE 1. THERMODYNAMIC PROPERTIES OF SOME COMPOUNDS AND IONS
OF THE SYSTEM U-O-H₂O AT 25° C.

(Heat and free energy of formation in kcal; entropy of substance in cal./deg.
Data from Latimer, 1952, except as noted)

Compound or Ion	ΔH^0	ΔF^0	S^0	State
UO ₃ · 3H ₂ O		[−376] ¹		Crystalline
UO ₂ · 2H ₂ O[UO ₂ (OH) ₂ · H ₂ O]	−446.2	[−399] ¹	[40.4] ¹	Crystalline
UO ₃ · H ₂ O	−375.4	−343	(33)	Crystalline
UO ₃	−291.6 ²	−273.1 ²	23.57	Crystalline
UO ₂	−259.2 ²	−246.6 ²	18.6	Crystalline
U(OH) ₄		(−351.6) ³		Crystalline
U(OH) ₃		(−263.2) ³		Crystalline
UO ₂ ²⁺	−250.4	−236.4	−17	Aqueous
UO ₂ ⁺	−247.4	−237.6	12	Aqueous
U(OH) ³⁺	−204.1	−193.5	−30	Aqueous
U ⁴⁺	−146.7	−138.4	−78	Aqueous
U ³⁺	−123.0	−124.4	−30?	Aqueous
H ₂ O	−68.317	−56.690	16.716	Liquid
O ₂	0.0	0.0	49.003	Gaseous
H ₂	0.0	0.0	31.211	Gaseous
OH [−]	−54.957	−37.595	−2.52	Aqueous

¹ Estimated by the author.

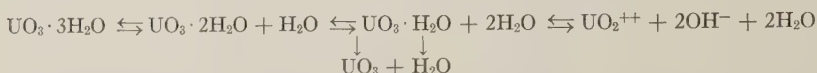
² Seaborg and Katz (1954, p. 174).

³ Estimated by Latimer.

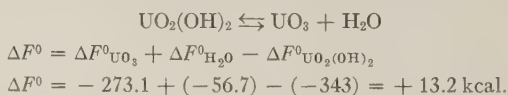
and from Seaborg and Katz (1954), with the exception of the bracketed values, which have been calculated by the present author. The method of calculation is described in the appendix.

Relations among the uranium (VI) compounds

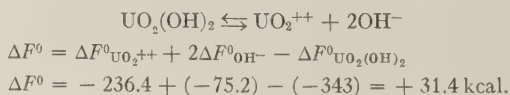
If $\text{UO}_3 \cdot 3\text{H}_2\text{O}$ is put into water, the following reactions among the known species are possible (coexistence at equilibrium of all the species listed is not implied):



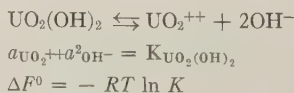
The monohydrate is shown ionizing to the uranyl and hydroxide ions because of the likelihood that $\text{UO}_3 \cdot \text{H}_2\text{O}$ is better expressed as $\text{UO}_2(\text{OH})_2$. The free energy changes of the various hydration reactions $\text{UO}_3 \cdot 3\text{H}_2\text{O} \rightleftharpoons \text{UO}_3 \cdot 2\text{H}_2\text{O} + \text{H}_2\text{O} \rightleftharpoons \text{UO}_3 \cdot \text{H}_2\text{O} + 2\text{H}_2\text{O}$ probably are small. This conclusion is based in part on analogy with the free energies of hydration of other compounds and in part on the fact that ΔF^0 for the formation of $\text{UO}_2(\text{OH})_2 \cdot \text{H}_2\text{O}$, calculated from ΔH^0 and an estimated value of ΔS^0 , corresponds closely to the value calculated on the assumption that the free energy change of hydration of $\text{UO}_2(\text{OH})_2$ is zero. (See appendix.) On the other hand, UO_3 seems definitely unstable relative to $\text{UO}_2(\text{OH})_2$:



There is also a large free energy change accompanying the ionization of $\text{UO}_2(\text{OH})_2$:



From this free energy change the activity product of $\text{UO}_2(\text{OH})_2$ can be calculated:

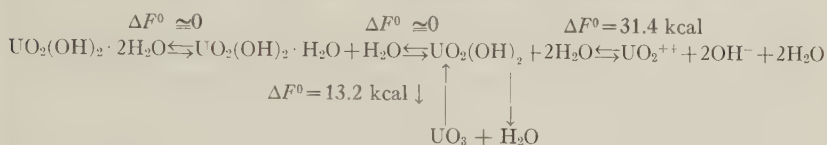


At 25 C, ΔF^0 (kcal) = $-1.364 \log K$ (Latimer, 1952, p. 8). Therefore:

$$31.4 = -1.364 \log a_{\text{UO}_2^{++}} + a_{\text{OH}^-}^2$$

$$a_{\text{UO}_2^{++}} + a_{\text{OH}^-}^2 = 10^{-23} \quad (1)$$

From these relations, the free energy changes of the various reactions of uranium (VI) in water can be summarized diagrammatically:



Therefore, it would seem that the various hydrated oxides have no very great tendency to transform one into the other and that several might be expected to coexist metastably for considerable periods of time. Anhydrous UO_3 would not be expected, even as a metastable phase. $\text{UO}_2(\text{OH})_2$ does not ionize freely and in the absence of complexes would dissolve perceptibly only in moderately acid solutions.

Relations among uranium (V) compounds

Uranium (V) can be formed metastably in water solution (Kraus, Nelson, and Johnson, 1949) as a more or less hydrolyzed UO_2^+ ion. Its rate of disproportionation into U^{4+} and UO_2^{++} ions, according to the reactions: $2\text{UO}_2^+ + 4\text{H}^+ \rightarrow \text{U}^{4+} + \text{UO}_2^{++} + 2\text{H}_2\text{O}$, is at a minimum between pH values of 2 and 4. The rate is finite, however, even in this range, so that the disproportionation may be a clue to the apparent lack of UO_2^+ compounds in nature.

Relations among the uranium (IV) compounds

In the system under consideration, free energy data are available only for the uranium (IV) compounds $\text{U}(\text{OH})_4$ and UO_2 . The reactions with water are:



The free energy change of the reaction on the left is:

$$\begin{aligned}
 \Delta F^0 &= \Delta F^0_{\text{U}(\text{OH})_4} - \Delta F^0_{\text{UO}_2} - 2\Delta F^0_{\text{H}_2\text{O}} \\
 \Delta F^0 &= -351.6 - (-246.6) - (-113.4) = +8.4 \text{ kcal.}
 \end{aligned}$$

Therefore, the hydroxide is definitely unstable with respect to the oxide, and, although the free energy relations give no information on rates, the hydroxide would not be expected to form and persist indefinitely but to change to the oxide. The instability of the uranium (IV) hydroxide is in accord with the instability of Am (IV), Th (IV), and Sn (IV) hydroxides. The hydroxide, however, probably forms metastably during any laboratory precipitation, and then changes to the oxide on standing, so that the measured solubility would be that of the hydroxide, rather than that of the oxide. The probable relations between oxide and hydroxide can be shown from a consideration of their activity products.

For the ionization of $\text{U}(\text{OH})_4$:

$$\begin{aligned}\text{U}(\text{OH})_4 &\rightleftharpoons \text{U}^{4+} + 4\text{OH}^- \\ \Delta F^0 &= \Delta F^0_{\text{U}^{4+}} + 4\Delta F^0_{\text{OH}^-} - \Delta F^0_{\text{U}(\text{OH})_4} \\ \Delta F^0 &= -138.4 + (-350.4) - (-351.6) = +62.8 \text{ kcal.}\end{aligned}$$

From this value of ΔF^0 , the activity product of $\text{U}(\text{OH})_4$ is:

$$\begin{aligned}a_{\text{U}^{4+}}a_{\text{OH}^-}^4 &= K_{\text{U}(\text{OH})_4} \\ \Delta F^0 &= -RT \ln K \\ 62.8 &= 1.364 \log a_{\text{U}^{4+}}a_{\text{OH}^-}^4 \\ a_{\text{U}^{4+}}a_{\text{OH}^-}^4 &= 10^{-46} = K_{\text{U}(\text{OH})_4}.\end{aligned}\quad (2)$$

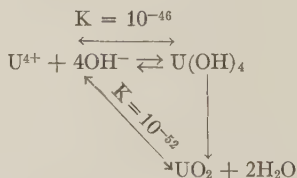
For the direct ionization of UO_2 :

$$\begin{aligned}\text{UO}_2 + 2\text{H}_2\text{O} &\rightleftharpoons \text{U}^{4+} + 4\text{OH}^- \\ \Delta F^0 &= \Delta F^0_{\text{U}^{4+}} + 4\Delta F^0_{\text{OH}^-} - \Delta F^0_{\text{UO}_2} - 2\Delta F^0_{\text{H}_2\text{O}} \\ \Delta F^0 &= -138.4 + (-150.4) - (-246.6) - 2(-56.7) = +71.2 \text{ kcal.}\end{aligned}$$

The activity product of UO_2 is:

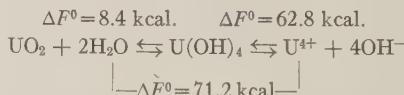
$$\begin{aligned}a_{\text{U}^{4+}}a_{\text{OH}^-}^4 &= K_{\text{UO}_2} \\ \Delta F^0 &= -RT \ln K_{\text{UO}_2} \\ 71.2 &= 1.364 \log K_{\text{UO}_2} \\ K_{\text{UO}_2} &= a_{\text{U}^{4+}}a_{\text{OH}^-}^4 = 10^{-52}\end{aligned}$$

When U^{4+} is precipitated from water solution, two paths seem possible:



If precipitation takes place at true equilibrium, the precipitate should be UO_2 , which has the smaller K . But experimentally it is almost impossible to avoid exceeding both K_{UO_2} and $K_{\text{U}(\text{OH})_4}$, and the metastable $\text{U}(\text{OH})_4$ would be expected to form more rapidly, changing later to UO_2 .

In summary:



Uranium (IV) would be expected to come out of solution as the hydroxide, and then change to the oxide, but the true equilibrium is between UO_2 and the ions.

Relations among the uranium (III) compounds

It seems unlikely that uranium (III) compounds would be found under natural conditions at low temperature (Latimer, 1952, p. 301), for the

U^{3+} ion is highly unstable with respect to the liberation of hydrogen from water and would be expected to react immediately to a higher valence.

Relations between the uranium (VI) and the uranium (IV) systems

In water solution, the uranium (VI) and uranium (IV) compounds can be considered to be connected through the UO_2^{++} and the U^{4+} ions. Under oxidizing conditions there is a tendency to transform U^{4+} to UO_2^{++} and, as a result, to shift the equilibria toward the formation of uranium (VI) compounds. Under reducing conditions the reverse is true. The relation can be expressed as an equation:

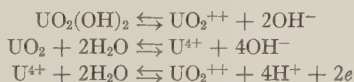


The free energy change can be calculated as before:

$$\begin{aligned}\Delta F^0 &= \Delta F^0_{UO_2^{++}} + 4\Delta F^0_{H^+} - \Delta F^0_{U^{4+}} - 2\Delta F^0_{H_2O} \\ \Delta F^0 &= -236.4 + (0) - (-138.4) - (-113.4) = +15.4 \text{ kcal.}\end{aligned}$$

In other words, at unit activity of all constituents, UO_2^{++} tends to reduce to U^{4+} .

Because the uranium (VI) system presumably goes into solution through the ionization of $UO_2(OH)_2$, and the uranium (IV) system through UO_2 , the three controlling reactions are:



The equilibrium relations are:

$$a_{UO_2^{++}} a_{OH^-}^2 = 10^{-23} \quad (1)$$

$$a_{U^{4+}} a_{OH^-}^4 = 10^{-52} \quad (2)$$

$$Eh = -E^0 + 0.03 \log \frac{a_{UO_2^{++}} a_{H^+}^4}{a_{U^{4+}}} \quad (3)$$

Equation 3 is the standard oxidation equation relating oxidation potential of the system (Eh) to the standard electrode potential (E^0) and the ionic ratios. Pourbaix (1949) gives a fuller discussion of this relation.

If $UO_2(OH)_2$ and UO_2 are in equilibrium, equations 1 and 2 hold. Then, dividing 1 by 2 and transforming:

$$\frac{a_{UO_2^{++}}}{a_{U^{4+}}} = 10^{29} a_{OH^-}^2 \quad (4)$$

and:

$$\log \frac{a_{UO_2^{++}}}{a_{U^{4+}}} = 29 + 2 \log a_{OH^-} \quad (5)$$

The a_{OH^-} can be related to the $p\text{H}$. Because

$$a_{\text{H}^+}a_{\text{OH}^-} = Kw = 10^{-14} \text{ at } 25^\circ\text{C.}$$

then:

$$a_{\text{OH}^-} = \frac{Kw}{a_{\text{H}^+}}$$

and:

$$\log a_{\text{OH}^-} = \log Kw - \log a_{\text{H}^+}.$$

By definition, $p\text{H} = -\log a_{\text{H}^+}$, so:

$$\log a_{\text{OH}^-} = p\text{H} - 14.$$

Substituting this relation in equation 5:

$$\log \frac{a_{\text{UO}_2^{++}}}{a_{\text{U}^{4+}}} = 29 + 2(p\text{H} - 14)$$

or:

$$\log \frac{a_{\text{UO}_2^{++}}}{a_{\text{U}^{4+}}} = 2 p\text{H} + 1. \quad (6)$$

Equation 3 can be rewritten to contain $p\text{H}$:

$$Eh = E^0 + 0.03 \log \frac{a_{\text{UO}_2^{++}}}{a_{\text{U}^{4+}}} - 0.12 p\text{H}$$

Substituting the value from equation 6 for $\log a_{\text{UO}_2^{++}}/a_{\text{U}^{4+}}$

$$Eh = -E^0 + 0.03(2 p\text{H} + 1) - 0.12 p\text{H}$$

and:

$$Eh = -E^0 + 0.03 - 0.06 p\text{H}.$$

Therefore, Eh is a linear function of $p\text{H}$ at conditions of equilibrium for UO_2 and $\text{UO}_2(\text{OH})_2$.

Substituting the numerical value of E^0 , which is -0.334 volt at 25°C . (Latimer, 1952, p. 301), the simple equation is obtained:

$$Eh = 0.364 - 0.06 p\text{H}. \quad (7)$$

Figure 1 shows the boundary between the stability fields of the two compounds, calculated from equation 7. Above the boundary $\text{UO}_2(\text{OH})_2$ is the stable solid phase; below, UO_2 . Because of the small free energy differences between the various uranium (VI) hydrates, it is not unlikely that any one or a combination of them may form and persist. On the other hand, the uranium (IV) oxide is definitely stable with respect to the hydroxide, which, if formed, would be expected to change at a finite rate to UO_2 . The boundary shown for the stability of water apparently precludes the possibility of occurrence of uranium (III) compounds; the stability field of $\text{U}(\text{OH})_3$ is more than 0.5 volt below this

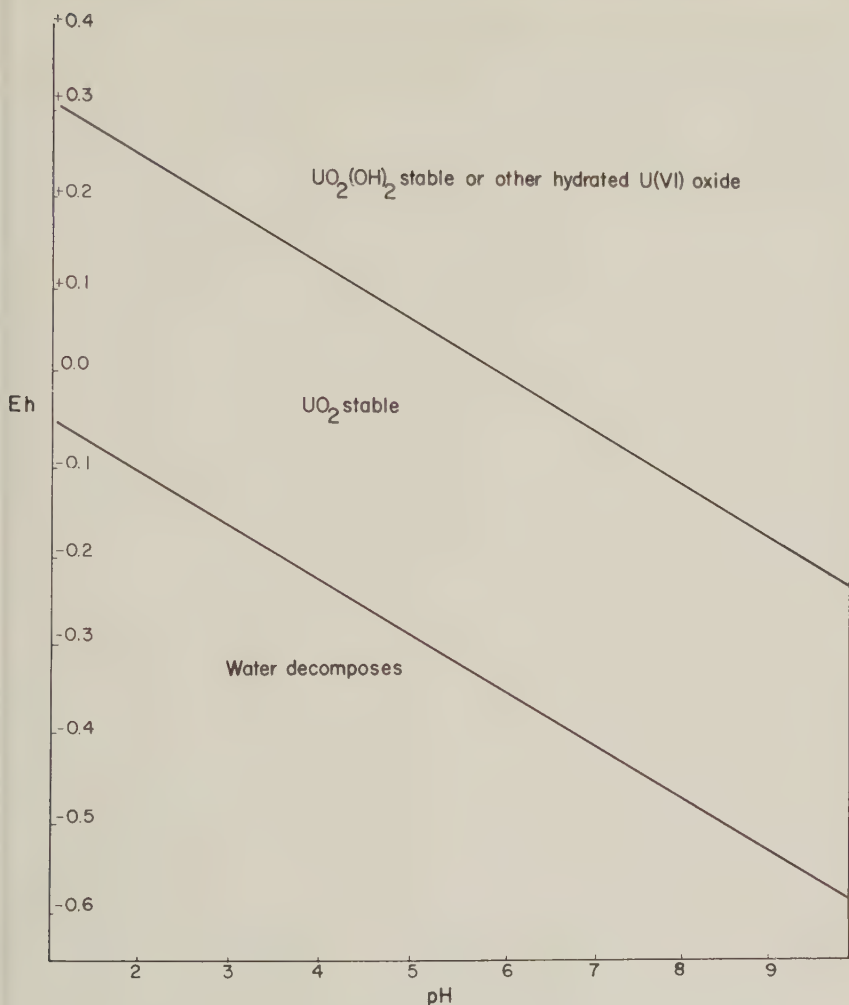


FIG. 1. Fields of stability of UO_2 and of hydrated U^{+6} oxides.

boundary, which practically assures that $\text{U}(\text{OH})_3$ would decompose water at a finite rate.

Figure 2 shows the same stability fields with contours of the activity of UO_2^{++} ion superimposed.¹ The activity is significant ($>10^{-6}$) only in mildly oxidizing acid solutions.

In Fig. 3 contours of the activity of U^{4+} ion are shown. Activity ex-

¹ For details of the construction of such contoured diagrams, see Krumbein and Garrels (1952) or Pourbaix (1949).

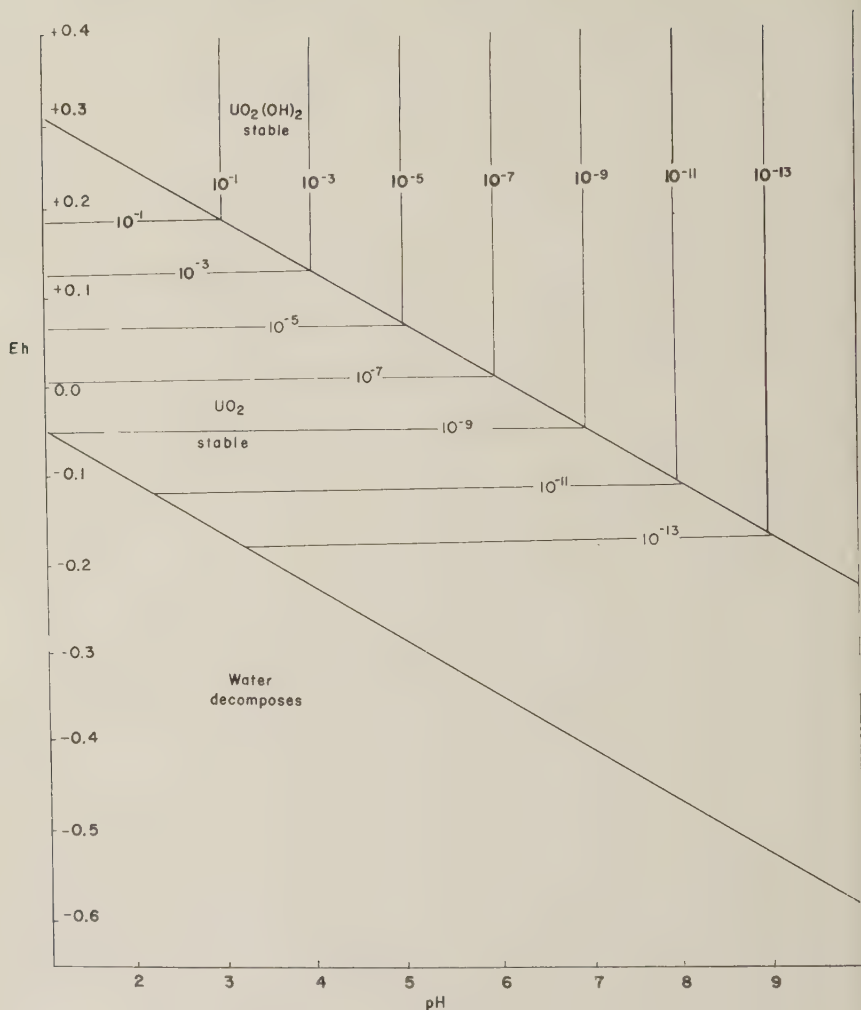


FIG. 2. UO_2^{++} ion activity in equilibrium with $\text{UO}_2(\text{OH})_2$ and UO_2 .

ceeds 10^{-6} only at pH values of 2.5 or less.

Figure 4 shows contours of the sum of $a_{\text{U}^{4+}}$ and $a_{\text{UO}_2^{++}}$ and re-emphasizes the low activity of either ion in very weakly acid or alkaline solutions.

Figure 5, a plot of the ratio of UO_2^{++} activity to U^{4+} activity, shows that the contribution of U^{4+} ion is relatively insignificant except under acid reducing conditions. In other words, UO_2^{++} ion activity far exceeds that of U^{4+} under most conditions, even in the field of stability of UO_2 .

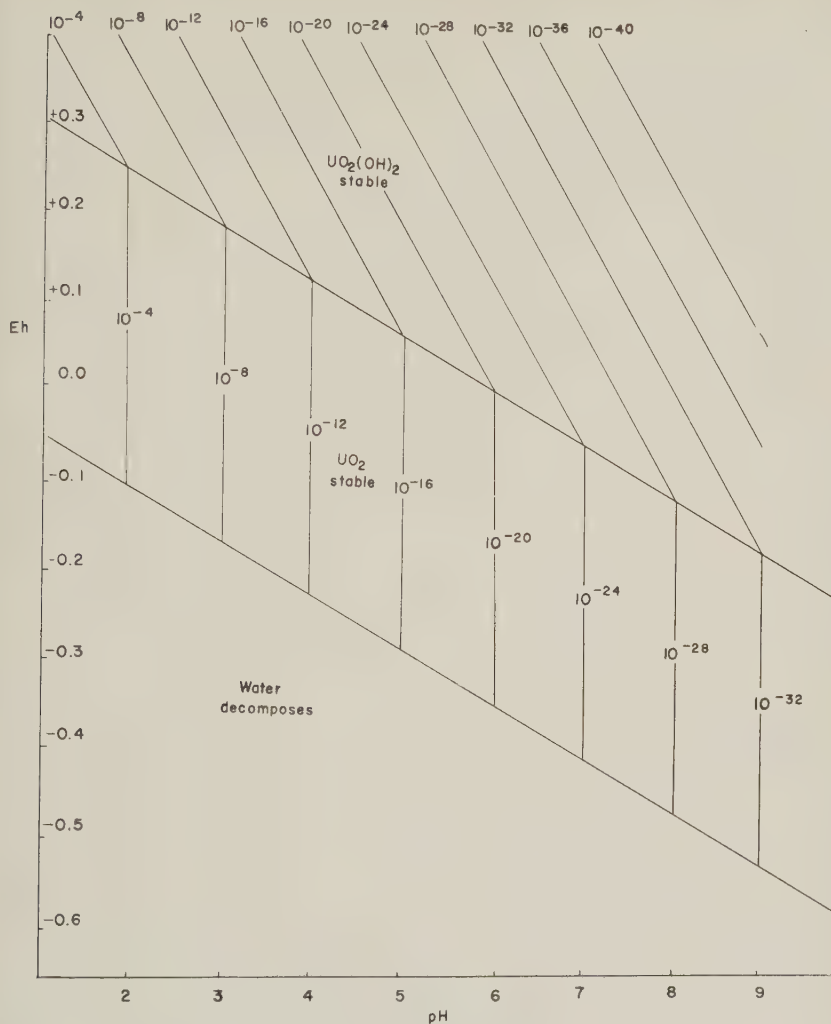


FIG. 3. U^{4+} ion activity in equilibrium with $UO_2(OH)_2$ and UO_2 .

Relation of vanadium and uranium oxide stability fields

A study of the fields of stability of the vanadium oxides already has been made (Garrels, 1953). In Fig. 6 the fields of the uranium and vanadium oxides are shown together. Contours have been drawn to show conditions under which the total activity of various vanadium ions [$\Sigma a_{V^{++}} + a_{V^{3+}} + a_{VO^{++}} + a_{V(OH)_4^{+}}$] is appreciable (10^{-2}) and negligible (10^{-6}). Similar treatment has been accorded $\Sigma a_{UO_2^{++}} + a_{U^{4+}}$.

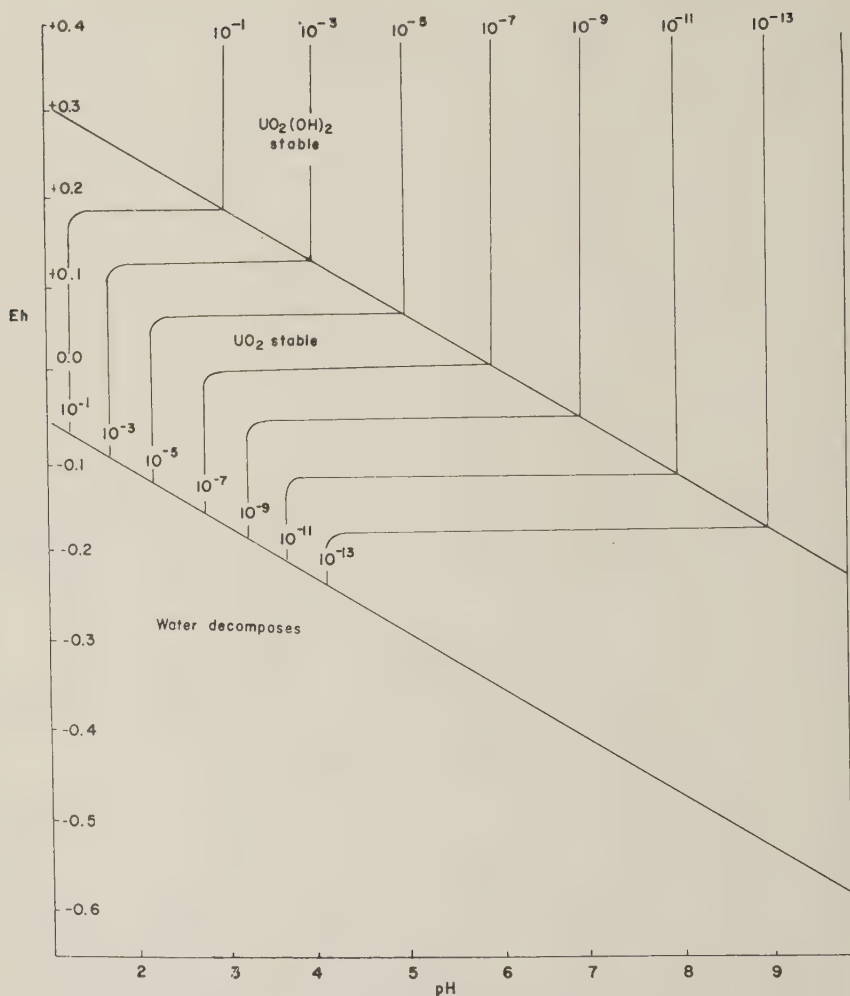


FIG. 4. Sum of activities of UO_2^{++} and U^{4+} ions in equilibrium with $\text{UO}_2(\text{OH})_2$ and UO_2 .

DISCUSSION AND INTERPRETATION

It is possible to draw a theoretical and partly hypothetical diagram showing overall Eh - pH stability relationships for an aqueous system containing the chief minerals of the various deposits on the Colorado Plateaus. (See Fig. 7.)

Fields 1 to 5 on this diagram have reasonable validity in that they actually have been calculated from thermodynamic data for the chemical compounds. Fields 6 and 7 are very highly speculative. To delimit

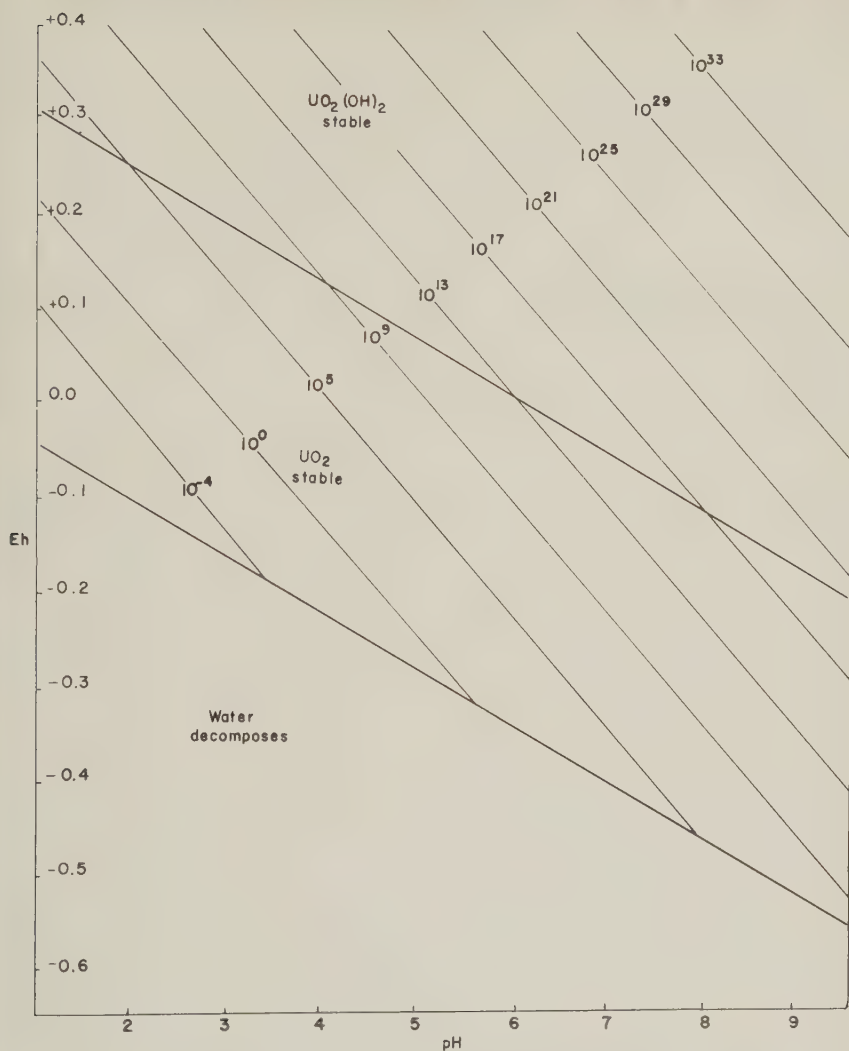


FIG. 5. Ratio of UO_2^{++} and U^{4+} ions in equilibrium with $\text{UO}_2(\text{OH})_2$ and UO_2 .

the stability fields of the various sulfides it has been necessary to make an assumption as to composition of the solutions. The assumption is that total sulfur ($\text{SO}_4^- + \text{H}_2\text{S} + \text{HS}^- + \text{S}^-$) is 0.1 mol per liter; this seems not unreasonable in that it is of the order of magnitude of total sulfur in mine water, which should be somewhat comparable to those of a naturally oxidizing ore deposit. Furthermore, a decrease of total sulfur to 0.001 molar would not change the pattern significantly.

The various fields delimited by the boundaries represent the best in-

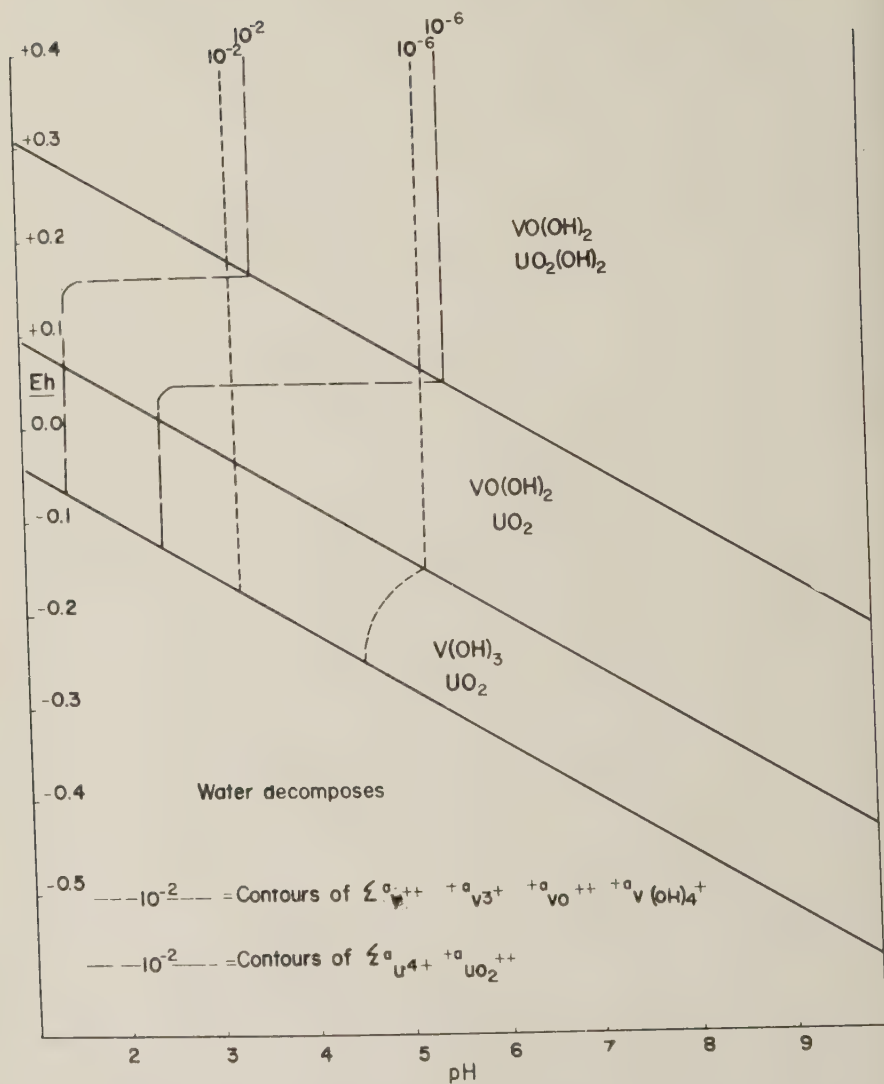


FIG. 6. Composite diagram showing fields of stability of some uranium and vanadium oxides and hydroxides.

terpretation possible at the present time as to stable mineral assemblages. Perhaps, to illustrate the kinds of changes expected as a result of oxidation of the most reduced assemblage, the best device is a discussion of the progressive changes expected as the oxidation potential is increased, carrying this original assemblage upward through the various fields.

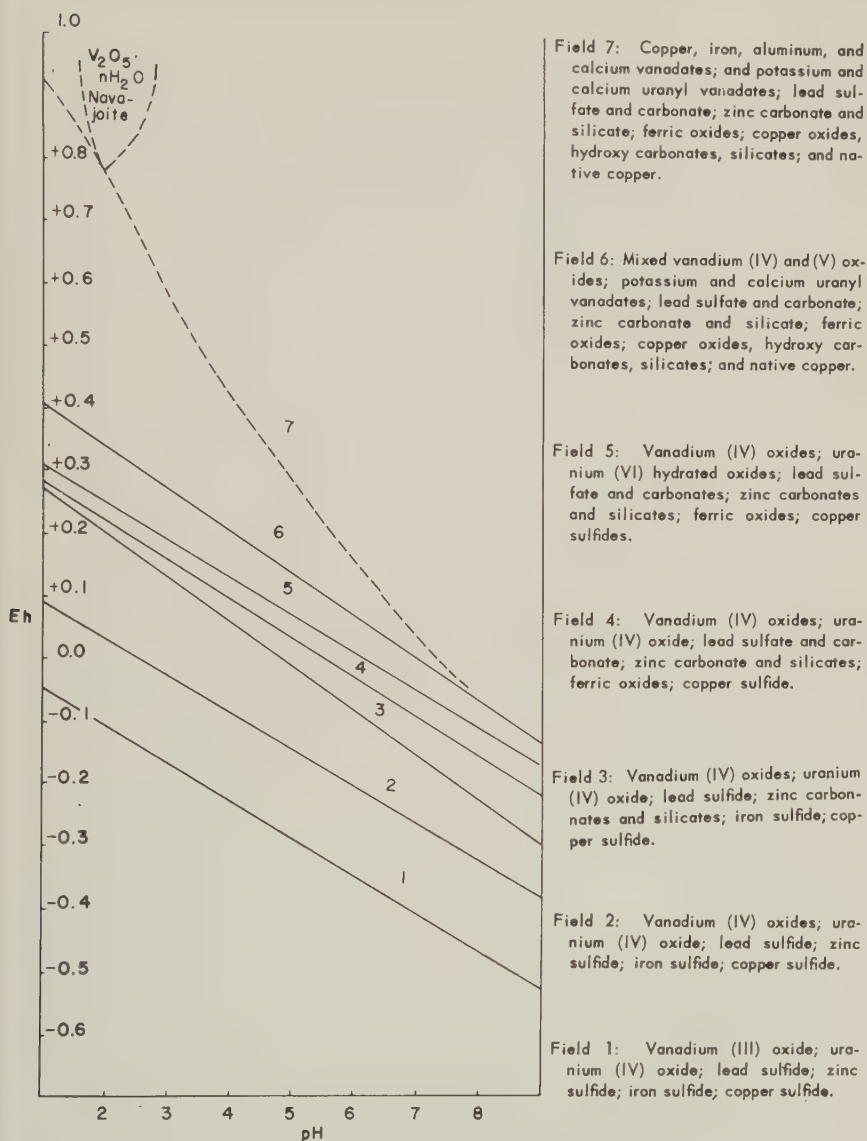


FIG. 7. Summary of information on stability relations of some major minerals of the Colorado Plateaus.

Field 1 is characterized by vanadium (III) oxides or hydroxides; uranium (IV) oxide; and zinc, lead, copper, and iron sulfides. Mineralogically this might represent a mineral association of montroseite, uraninite, galena, sphalerite, covellite, and pyrite. The first of these to oxidize

would be montroseite, and a field (field 2) presumably exists in which a vanadium (IV) oxide is stable in association with uraninite and the metal sulfides. Further increase in the oxidation of the environment through fields 3, 4, and 5 up into field 6, presumably would result in the oxidation in sequence of sphalerite, galena, pyrite, uraninite, and copper sulfide. In essence, then, the upper boundary of field 5 would seem to represent the most oxidizing conditions under which sulfide ion could resist oxidation up to sulfate. Zinc sulfide dissociates in water solution more easily than lead sulfide, which in turn dissociates more easily than copper sulfide; this explains the sequential oxidation of the sulfides, with sphalerite tending to decompose at lower *Eh* values. The exact position of pyrite is not known, although studies of the relative *rate* of oxidation (Koch and Grasselly, 1951) suggest that its ease of oxidation, at least, is comparable to that of other sulfides.

Above field 5 the relations are highly hypothetical, and no good data are known for the actual calculation of the stabilities of any of the uranium-vanadium compounds. Relations among some of the oxidized copper and lead compounds are known, and the fields of stability have been delimited (Garrels, 1954), but it seems unnecessary to attempt to show detailed relationships among them because their uranium-vanadium counterparts have not been worked out. The dashed line separating fields 6 and 7, however, represents a rough boundary interpreted from the work of Ducret (1951, p. 729-737) on the vanadium (IV)-(V) oxidation potential. Field 7 is the area in which vanadium exists as a complex series of vanadate ions, and where the ratio of these ions, carrying vanadium (V), to ions with quadrivalent vanadium (VO^{++}), is large (greater than 10). Field 6 on the other hand is an area in which the ratio of vanadium (IV) to vanadium (V) is significant and an area in which Ducret (1951, p. 729-737) found a whole series of vanadium IV-V oxides of variable composition. Therefore, it seems reasonable to assign to field 6 the complex mixture of natural vanadium (IV) and (V) oxides called corvusite and to field 7 the various metal-uranyl vanadates and metal vanadates such as carnotite, tyuyamunite, hewettite, pascoite, rossite, and others. One special point should be made in passing; at a *pH* of approximately 2, vanadium changes from an anionic role to a cationic one, from vanadate to the vanadyl (VO_2^+) ion (Ducret, 1951, p. 714). In this general *pH* range, during the transition, hydrated V_2O_5 precipitates; therefore, it seems likely that navajosite, the naturally occurring V_2O_5 hydrate (Weeks, Thompson, and Sherwood, 1954), is an excellent indicator of rather strongly acid oxidizing solutions.

On the basis, then, of the estimation of stability fields as shown in field 7, a "narrative" interpretation of the oxidation of a primary mon-

troseite, uraninite, pyrite, sphalerite, galena, covellite ore can be attempted. Under ordinary ground-water conditions the environment is reducing and alkaline (Garrels, 1953, pp. 1263-1264). On the other hand, atmospheric oxygen brought into the system is a strong oxidizing agent, and even traces of oxygen tend to raise the oxidation potential to plus values of several tenths of a volt. The effect is to superimpose a strongly oxidizing environment, represented perhaps by fields 6 and 7, on the original reduced-mineral assemblage. The tendency is to pull all the compounds up to highly oxidized species. If equilibrium were attained instantaneously, the original association would jump to the associations of fields 6 and 7. The oxygen, however, is probably supplied slowly during weathering, and the rate of reaction with the various species would be expected to differ markedly. If considered entirely from the oxidation potential standpoint, that is, if the rates are entirely functions of the difference in potential between the environment and the upper limit of mineral stability, then it would be expected that the vanadium oxides would weather to vanadium (IV) compounds before the sulfides were significantly attacked and that uraninite should oxidize to uranium (VI) compounds when the sulfides change to sulfate, oxides, and carbonates. Actual experiment is necessary, however, to assess the relative effect of the potential versus the rate characteristics of the individual species.

When the sulfides become unstable, sulfide ion is converted to sulfate, and the freed metal ions become involved in a variety of reactions depending upon the relative stabilities of the various solids that can form with the chief anionic constituents of the oxidized solutions. Lead tends to form slightly soluble sulfates and carbonates; zinc to form moderately soluble carbonates and silicates; copper to form a variety of oxides, carbonates, and hydroxy-carbonates, as well as native copper and copper silicate. The iron from pyrite tends to hydrolyze into hematite or various hydrated ferric oxides.

The vanadium, after it reaches the quadrivalent stage, probably oxidizes through a complex series of vanadium (IV) and (V) oxides (corvusite). As more and more of the vanadium reaches the quinquevalent state it tends to go into vanadates. Any uranium (VI) possibly present briefly in the pre-vanadate stage as uranium (VI) oxides tends to be converted into potassium or calcium uranyl vanadates. Vanadium in excess of the amount necessary to form these uranyl compounds would tend to precipitate as simple metal vanadates.

SUMMARY AND CONCLUSION

The present information on the fields of stability of the minerals of the Colorado Plateaus-type deposits is quite consistent with an interpre-

tation that the original ores were species containing "sensitive" elements in their lower valence states, and that the great complexity of the mineralogy, as now observed, can be attributed to the superimposition of oxidation, of various degrees of completeness, through the primary agency of atmospheric oxygen. It should also be clearly emphasized that the present picture may also be interpreted on the basis of the influence of a variety of original environments acting at the time of deposition, or by various combinations of these two major conceptual schemes. A determination of the actual processes can be made by extensive study of the paragenesis of the minerals and of the geologic occurrence of the ores. According to the "weathering hypothesis," oxidation should have taken place only in those places accessible to atmospheric oxygen. It should not be difficult to assess the validity of this hypothesis if field studies are made with the question in mind.

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APPENDIX

*Calculation of free energy of formation
for uranium compounds*

Two methods have been used to calculate the values in brackets in Table 1. The first is by estimation of entropy values if ΔH^0 is known, and then using the relation $\Delta F^0 = \Delta H^0 - T\Delta S^0$; the second by using the

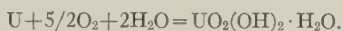
assumption that the hydration reaction is essentially an equilibrium process, so that the free energies of formation of the products is equal to the sum of the free energies of formation of the reactants.

For $\text{UO}_3 \cdot 2\text{H}_2\text{O}$ both methods can be used. ΔH^0 is known; S^0 can be estimated by the methods outlined by Latimer (1952, pp. 359–369).

Because uranium (VI) in water solution gives the stable UO_2^{++} ion, it seems likely that $\text{UO}_3 \cdot 2\text{H}_2\text{O}$ is better expressed as $\text{UO}_2(\text{OH})_2 \cdot \text{H}_2\text{O}$. According to Latimer's values for the entropies of elements in compounds, uranium is 16, oxygen is 3, OH^- is 4.5, H_2O is 9.4.

U	16
2O	6
2OH ⁻	9
H ₂ O	9.4
<hr/>	
40.4 = $S^0 \text{UO}_2(\text{OH})_2 \cdot \text{H}_2\text{O}$	

ΔS^0 can then be obtained from the reaction:



Using the entropies of the elements (Table 1):

$$\begin{aligned} \Delta S^0 &= S^0_{\text{UO}_2(\text{OH})_2 \cdot \text{H}_2\text{O}} - S^0_{\text{U}} - 5/2 S^0_{\text{O}_2} - 2 S^0_{\text{H}_2\text{O}} \\ \Delta S^0 &= 40.4 \quad \quad \quad - 16.0 - 122.5 - 62.4 = -160.5 \end{aligned}$$

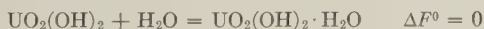
Then:

$$\Delta F^0 = \Delta H^0 - T\Delta S^0$$

At 25° C., ΔH^0 for the formation of $\text{UO}_2(\text{OH})_2 \cdot \text{H}_2\text{O}$ is -446.2 kcal (Table 1). Then:

$$\Delta F^0 = -446,200 - (298 \times -160.5) = 398,400 \text{ cal} = 398.4 \text{ kcal}.$$

For the second method, the assumption is made:



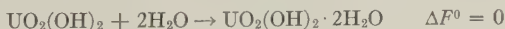
$$\Delta F^0_{\text{UO}_2(\text{OH})_2} + \Delta F^0_{\text{H}_2\text{O}} = \Delta F^0_{\text{UO}_2(\text{OH})_2 \cdot \text{H}_2\text{O}}$$

From Table 1:

$$-343 + (-56.7) = -399.7 \text{ kcal} = \Delta F^0_{\text{UO}_2(\text{OH})_2 \cdot \text{H}_2\text{O}}$$

Therefore the values by the two methods check within 1.3 kcal, or less than 0.4 per cent difference.

For $\text{UO}_2 \cdot 3\text{H}_2\text{O}$ no value of ΔH^0 is available, and the bracketed value in Table 1 is based on the second method:



$$\Delta F^0_{\text{UO}_2(\text{OH})_2} + \Delta F^0_{2\text{H}_2\text{O}} = \Delta F^0_{\text{UO}_2(\text{OH})_2 \cdot 2\text{H}_2\text{O}}$$

Substituting ΔF^0 values from Table 1:

$$-343 + (-33.4) = -376.4 \text{ kcal} = \Delta F^0_{\text{UO}_2(\text{OH})_2 \cdot 2\text{H}_2\text{O}}$$

THE PECTOLITE-SCHIZOLITE-SERANDITE SERIES*

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ABSTRACT

A study of the pertinent recorded analyses of pectolite, schizolite, and serandite, indicates that they are members of an isostructural series from pectolite ($4\text{CaO} \cdot \text{Na}_2\text{O} \cdot 6\text{SiO}_2 \cdot \text{H}_2\text{O}$ or $\text{Ca}_2\text{NaSi}_3\text{O}_8(\text{OH})$) to serandite ($4\text{MnO} \cdot \text{Na}_2\text{O} \cdot 6\text{SiO}_2 \cdot \text{H}_2\text{O}$ or $\text{Mn}_2\text{NaSi}_3\text{O}_8(\text{OH})$), another example of a series in which calcium and manganese proxy each other. The only recorded analysis of serandite is that of a calcian serandite. Schizolite is a manganoan pectolite and should not be rated as a species.

The specific gravity and indices of refraction for the calcium and for the manganese end members are:

$$\begin{aligned} \text{Pectolite, } \text{Ca}_2\text{NaSi}_3\text{O}_8(\text{OH}), \quad G &= 2.86; \quad \alpha = 1.595, \\ &\quad \beta = 1.605, \quad \gamma = 1.633. \\ \text{Serandite, } \text{Mn}_2\text{NaSi}_3\text{O}_8(\text{OH}), \text{ (by extrapolation)} \quad G &= 3.32; \\ &\quad \alpha = 1.680, \quad \beta = 1.682, \quad \gamma = 1.705. \end{aligned}$$

INTRODUCTION

The pectolite-schizolite-serandite series is an example of an isostructural series in which bivalent manganese (I.R. 0.80) proxies for calcium (I.R. 0.99) at least to an extent of 77 per cent. The calcite-rhodochrosite series is even more complete for it indicates "complete ionic substitution of Mn^{++} to Ca^{++} in nature." as expressed by Kulp, Kent, and Kerr (1951) or, as stated earlier by Kulp, Wright, and Holmes (1949): "Therefore, it seems that the substitution of Ca^{++} for Mn^{++} is continuous for rhodochrosite to calcite." These conclusions confirm the earlier work of Krieger (1930). The wollastonite-bustamite series is another example in which manganese (plus a little ferrous iron) proxies the calcium in wollastonite to the extent of at least 70 per cent, with retention of the wollastonite structure (Schaller).

The maximum content of $\text{MnO} + \text{FeO}$ so far found, in a bustamite from Australia, is about 28 per cent MnO with 8 per cent FeO . Several additional bustamites from other localities contain almost as much manganese and iron (Schaller). For axinite the ratio of CaO to $\text{FeO} + \text{MnO} + \text{MgO}$ was formerly held to be constant (Schaller, 1911) but recent studies by Milton, Hildebrand, and Sherwood (1953) show it to be variable.

In rhodonite and pyroxmangite the amount of calcium proxying for manganese is variable but always small. The maximum content of CaO in rhodonite is about 11 per cent (Schaller, 1938, p. 582). The so-called

* Publication authorized by the Director, U. S. Geological Survey.

"high lime rhodonites" listed in standard reference books are either bustamite, johannsenite, or a mixture of rhodonite and johannsenite (Schaller, 1938, p. 580). In other calcium-manganese minerals, such as inesite (Glass and Schaller, 1939) and johannsenite (Schaller, 1938) the content of CaO is constant and calcium and manganese do not proxy each other.

In all three of the series mentioned in which the proxying of manganese for calcium is complete or nearly so, the almost manganese-free calcium end member is by far the commonest and most abundant. For those series (rhodonite, pyroxmangite) in which the manganese end member is the commonest and most abundant, calcium seems to be always minor in amount.

That serandite, the manganese richest member of the pectolite-

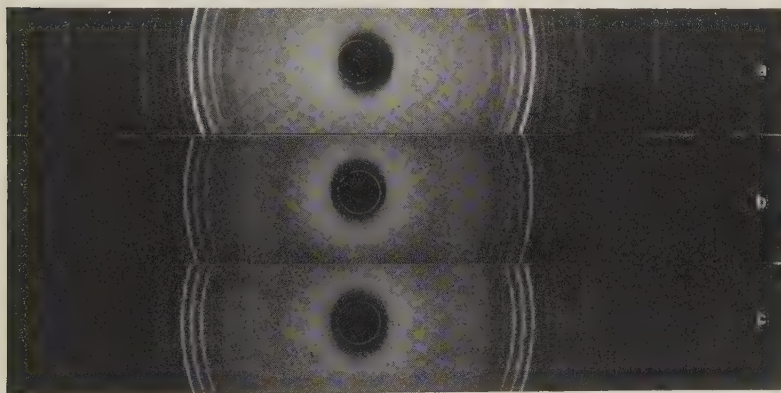


FIG. 1. (a) Pectolite; (b) Schizolite; (c) Serandite.

schizolite-serandite series is a pectolite in which manganese proxies calcium to an extent greater than a 1:1 ratio, was shown by Machatschki (1932). Schizolite is intermediate between pectolite and serandite and the close morphological relationship of the triclinic crystals of schizolite and pectolite was shown by Peacock (1935) and by Ito (1939).

The similarity of the x-ray powder patterns of the three minerals is shown in Fig. 1 and the shifts in the positions of the lines in Table 1. Many pectolites contain small quantities of manganese, as well as iron, though it is believed that the MnO content of the manganpectolite from Magnet Cove, described by Williams (1891) and reported to be 4.25 per cent MnO, is much too high, like the MnO and FeO percentages given by him for the wollastonite and natroxonotlite from Potash Sulphur Springs, Arkansas (Schaller, 1950). That the content of MnO in the manganpectolite from Arkansas is not as high as reported is also indi-

TABLE 1. POWDER DATA FOR THE COMPARISON OF PECTOLITE, SCHIZOLITE, AND SERANDITE

Pectolite		Schizolite		Serandite	
<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>
7.83	5	7.73	mw	7.55	ms
7.03	5	6.92	mw	6.75	ms
5.50	5	5.39	mw	5.24	mw
3.90	6	3.85	ms	3.77	ms
3.52	5	3.47	mw	3.38	mw
3.33	6	3.27	ms	3.19	s
3.10	8	3.06	ms	3.00	s
2.92	10	2.89	s	2.85	s
2.74	6	2.69	ms	2.62	ms
2.60	6	2.56	ms	2.51	ms
2.30	6	2.27	ms	2.21	ms
2.17	6	2.15	ms	2.12	mw

s=strong.

ms=moderately strong.

mw=moderately weak.

cated by the value of its specific gravity, namely, 2.845, as given by Williams, which is lower than the specific gravity (2.86) of pectolite free from manganese.

X-RAY PATTERNS

X-ray diffraction patterns of these minerals were taken some years ago by W. E. Richmond, formerly of the U. S. Geological Survey, and more recently by Fred A. Hildebrand.

The specimens for which patterns were obtained, are as follows:

Pectolite from Bergen Hill, New Jersey, U.S.N.M. 82452. Film No. 5502.

Manganpectolite from Magnet Cove, Arkansas, U.S.N.M. R-3097. Film No. 240.

Schizolite from Julianehaab, Greenland, U.S.N.M. 95502. Film No. 5752.

Serandite from Los, French Guinea, U.S.N.M. 96515. Film No. 5739.

From a comparison of their patterns, C. L. Christ and J. M. Axelrod, of the U. S. Geological Survey, conclude that the same general pattern prevails and that all four samples are isostructural. The patterns of pectolite and of manganpectolite are identical; those of schizolite and of serandite contain some difference in line position and line intensity. However, it seems very likely that these differences can be ascribed to the differences in chemical composition. The patterns for schizolite and for serandite are very similar; their differences are less than their differences from the patterns of pectolite. But the overall similarity is retained and it must be concluded, on the basis of their powder patterns, that pectolite, manganpectolite, schizolite, and serandite form an isostructural series.

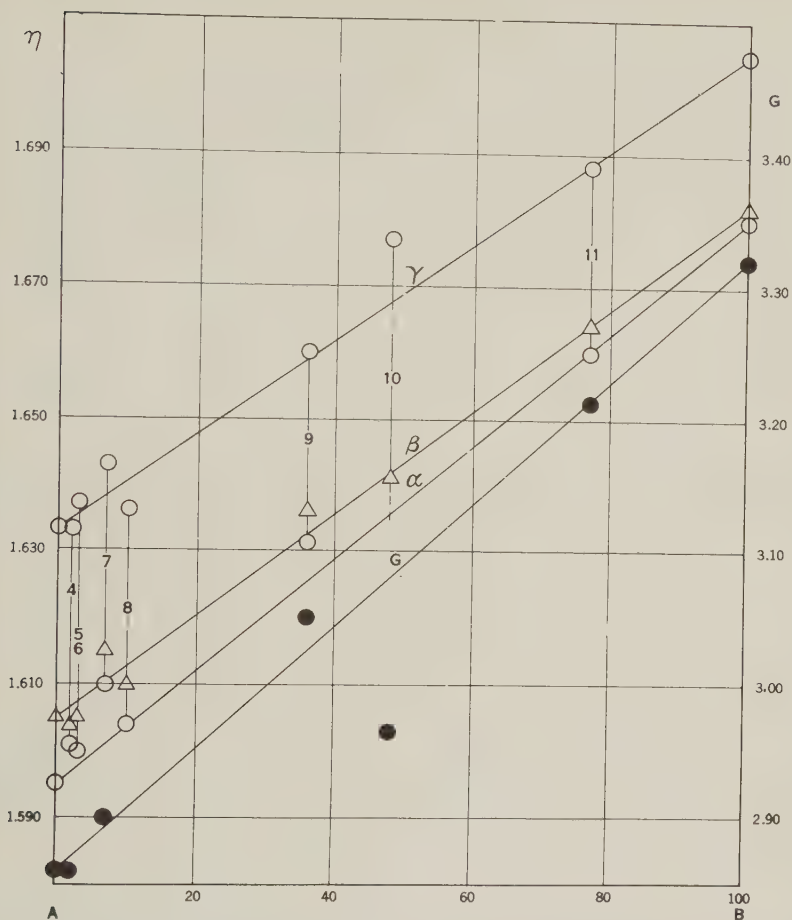


FIG. 2. Variation curves for G (specific gravities) and n (indices of refraction α , β , γ) for the pectolite-schizolite-serandite series. The values for alpha and gamma are represented by circles whereas those for beta are represented by triangles, so as to avoid confusion. Solid dots represent specific gravities.

A. Pectolite. $\text{Ca}_2\text{NaSi}_3\text{O}_8(\text{OH})$.

B. Serandite. $\text{Mn}_2\text{NaSi}_3\text{O}_8(\text{OH})$.

The powder data given in Table 1 were kindly furnished by Fred A. Hildebrand and are given here to show the isostructural relationship between pectolite, schizolite, and serandite. Measurements for d were made with a *m.m.* scale and I was estimated visually for schizolite and serandite. Corrections which would make very minor changes in d were not considered.

The patterns of the three minerals shown in Fig. 1 were taken with Debye Scherrer powder cameras (114.59 mm. diameter), FeK_α (Mn filter), $\lambda = 1.9373\text{\AA}$.

COMPILATION OF PROPERTIES

The available pertinent literature data on the properties of pectolite, schizolite, and serandite are shown in the following compilation (Table 2) and the variation curves for specific gravity and for the indices of refraction are given in Fig. 2. The component weight percentages are calculated on the basis of the determined values for MnO and FeO. The Ca-component is then obtained by difference. Both the specific gravities and the indices of refraction increase with increasing amounts of manganese. The continuous shift of the lines of the x-ray patterns has been given in Table 1.

The data are meager and there is little assurance that the physical properties were always determined on the actual samples analyzed. For example the three analyses of schizolite from Greenland (No. 9 in Table 1) given by Bøggild show considerable variation in the percentages of MnO (9.84, 11.69, and 12.90), and correspond to 32, 35, and 40 weight per cent of the calcium-free manganese and iron end members. The specific gravity of the mineral is given as within the range 2.97–3.13. The only indices of refraction of schizolite found in the literature are those given by Larsen (1921) for an unanalyzed specimen in the Harvard collection. The values plotted in Fig. 2 for schizolite are the average of the available data.

For pectolite, with less than one per cent of the calcium-free manganese and iron end member, Harada (1934) gives the indices of refraction for three analyzed samples (average given in column 3, Table 2). He also gives the indices for three additional samples not analyzed. His values agree very closely with those given in Larsen's Tables.

	α	β	γ
Harada analyzed	1.595	1.604	1.632
	1.594	1.603	1.631
	1.595	1.605	1.633
Harada not analyzed	1.595	1.604	1.633
	1.596	1.605	1.635
	1.594	1.604	1.632
Larsen's Tables, 1st ed.	1.595	1.606	1.633 (p. 118)
	1.595	1.606	1.634 (p. 216)
Larsen's Tables, 2nd ed.	1.595	1.604	1.633 (p. 110)
Average	1.595	1.605	1.633

TABLE 2. COMPILATION OF DATA ON THE PECTOLITE-SCHIZOLITE-SERANDITE SERIES

Reference Locality	Pectolite					
	1 —	2 Moravia	3 Japan	4 Ontario	5 New Jersey	6 Russia
Ca-comp.	100	100	100	98	97	96
Mn(Fe)-comp.	0	0	0	2	3	4
% MnO+FeO	0.00	0.00	0.15	0.76	1.12	1.53
α	1.595	1.600	1.595	1.601	1.600	1.600
β	1.605	—	1.604	1.604	1.605	—
γ	1.633	1.632	1.632	1.633	1.636	1.638
B	.038	.032	.037	.032	.036	.038
2V	63 ^a	—	60 ^o	—	50 ^o	—
G	2.86	—	2.86	2.86	—	—
SiO ₂	54.23	52.73	52.99	53.28	53.80	54.02
CaO	33.74	32.78	33.89	33.41	33.20	32.20
MnO	—	0.00	—	.33	.12	1.53
FeO	—	.05 ^b	.15	.43 ^b	1.00	—
Na ₂ O	9.32	7.97	8.97	9.14	9.01	8.88
H ₂ O	2.71	4.70	3.33	2.70	2.94	3.00
Etc.	—	1.86	.56	.67	—	.36
	100.00	100.09	99.89	99.96	100.07	99.99

^a Computed.^b Given as Fe₂O₃ but changed to its equivalent FeO where both iron oxides were not separately determined.

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TABLE 2. COMPILATION OF DATA ON THE PECTOLITE-SCHIZOLITE-SERANDITE SERIES—Continued

Reference Locality	Pectolite		Schizolite		Serandite	
	7 Russia	8 New Jersey	9 Green- land	10 Russia	11 French Guinea	12 —
Ca-Comp.	93	90	64	52	23	0
Mn(Fe)-Comp.	7	10	36	48	77	100
% MnO+FeO	2.60	3.86	13.99	18.66	30.32	39.16
α	1.610	1.604	1.631	—	1.660	1.680
β	1.615	1.610	1.636	1.641	1.664	1.682
γ	1.643	1.636	1.660	1.677	1.688	1.705
B	.033	.032	.029	—	.028	.025
2V	53°	—	47°	51°	36°	33° ^a
G	2.90	—	3.05 ^b	2.965 ^b	3.215	3.32
SiO ₂	50.34	52.04	51.19	54.84	48.72	49.79
CaO	32.36	31.15	20.97	14.21	10.42	—
MnO	1.52	2.57°	11.48	17.78 ^d	28.99	39.16
FeO	1.08°	1.29	2.51	.88°	1.33	—
Na ₂ O	8.33	7.97	10.06	8.62	7.38	8.56
H ₂ O	3.65	3.07	1.39	1.28	2.67	2.49
Etc.	2.45	2.12	2.42	2.39	.69	—
	99.73	100.21	100.02	100.00	100.20	100.00

^a Computed.^b Average of the ranges given, 2.97–3.13 for column 9 and 2.955–2.974 for column 10. These last values are probably low due to presence of MnO₂.^c Includes 0.26 per cent ZnO.^d After deducting 9.35 per cent MnO₂ and recalculating to 100 per cent. Given as 15.92 per cent MnO and 9.35 per cent MnO₂.^e Given as Fe₂O₃ but changed to its equivalent FeO as both iron oxides were not separately determined.

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The atomic ratios are calculated for four representative analyses, namely pectolite No. 5, schizolites Nos. 9 and 10, and serandite No. 11. The results are shown in Table 3 (next page).

Summarizing the results:

	Si	Ca, Mn, etc.	Na, K	OH
Pectolite 5	2.99	2.03	0.97	1.09
Schizolite 9	2.93	2.01	1.12	.53
Schizolite 10	3.10	1.79	1.00	.48
Serandite 11	2.93	2.21	.88	1.06
Average	2.99	2.01	0.99	0.79

These ratios indicate the type formula $(Ca, Mn)_2 NaSi_3O_8(OH)$ for all these members of the series. The determinations of water in the schizolites seem to be too low.

TABLE 3. ATOMIC RATIOS OF SELECTED ANALYSES

	Pectolite 5 New Jersey		Schizolite 9 Greenland		Schizolite 10 Russia		Serandite 11 Fr. Guinea	
Si	2.993	2.99	2.930	2.93	3.098	3.10	2.912	} 2.932 2.93
Al	—	—	—	—	—	—	.020	
Ti	—	—	.019	} 2.013 2.01	.001	} 1.785 1.79	—	} 2.208 2.21
Fe'''	—	—	—		—		.001	
Ce	—	—	.009		—		—	
Y	—	—	.017		.027		—	
Fe''	.047	} 2.029 2.03	.121		.041		.067	
Mn	.005		.557		.845		1.466	
Mg	—		.004		—		.006	
Ca	1.977		1.286		.860		.668	
Sr	—	—	—	} 1.004 1.00	.004	} 1.004 1.00	—	} .876 .88
Ba	—	—	—		.007		—	
Na	.972	.97	1.117	1.12	.943		.854	
K	—	—	—	—	.061		.022	
OH	1.089	1.09	.529	.53	.482	.48	1.062	1.06

CONCLUSION AND NOMENCLATURE

The meager data here presented on the pectolite-schizolite-serandite series indicate that these minerals are isostructural and are members of a continuous series. As in the calcite-rhodochrosite series, and in the wolastonite-bustamite series, they present an example of manganese proxying for calcium, for the pectolite series up to 77 per cent of the manganese (plus a little iron) end member.

Those with dominant Ca are pectolite. If desired, those varieties with considerable manganese (but less than 50 per cent molecularly of the manganese end member), such as the schizolites, can be designated as manganoan pectolites. The term schizolite can then be discarded as an unnecessary species name. The statement by Peacock (1935, p. 109) that "Pectolite and the manganese pectolite, schizolite" should read: "Pectolite and the manganoan pectolite, schizolite." Serandite is the "manganese pectolite" and the name serandite is to be applied to those members of the series with more than 50 per cent molecularly of the manganese end member. The only recorded analysis of serandite is that of a calcian serandite.

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PIEZOBIREFRINGENCE IN DIAMOND*

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ABSTRACT

In this study the stress-birefringence behavior of diamond has been investigated. The phenomenon has been neglected by both classical and modern crystallographers. A theoretical investigation of the stress-optical tensor for the cubic system confirms Bhagavan-tam's results. A new and substantially improved method of measurement of the stress-optical effect was developed. A study of the effects of non-uniform loading upon the results of measurement was made. It has been confirmed that the diamond is virtually isotropic in its stress-birefringence effect. The dispersion of the constant q_{1212} throughout the range 4400 Å to 7700 Å is no greater than $\pm 1\%$. The relative retardation varies linearly with stress to pressures of 40,000 psi. No hysteresis was observable upon sudden application or removal of load, nor could permanent deformation be produced by prolonged stresses of the order of 40,000 psi. Diamond becomes negative uniaxial or biaxial under a single linear compression, depending on the direction of force. The stress-birefringent behavior of diamond is found to be compatible with the elastic properties and internal structure of the diamond crystal.

The term *piezobirefringence* is proposed as being more descriptive of the phenomenon than *photoelasticity*.

INTRODUCTION

The phenomenon of stress birefringence was discovered by Sir David Brewster in 1815 (1). His first studies were concerned with the stress-optical effect in jellies, but by 1818 he had investigated the effect in amorphous solids, and in isotropic, uniaxial, and biaxial crystals (2, 3). Brewster was the first to discuss stress birefringence in the diamond. The work of Brewster was entirely qualitative, but it inspired Fresnel (4, 5) and several less well-known scientists, to attempt a theoretical explanation. They contributed little, however, toward any general theory. Neumann in the 1840's (6) founded a mathematical explanation of the observed behavior of non-crystalline substances, based on the strain-dependence of the birefringence. Maxwell in 1852 (7) announced a similar theory, based on the stress dependence. Though developed independently, both theories arrived at analogous results. Both are very useful today in the engineering applications of stress birefringence to the study of stress and strain in materials such as glass and lucite.

Wertheim, in the early 1850's, was the earliest to investigate quantitatively the stress-optical behavior of crystals (8, 9). Despite several omis-

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sions and misinterpretations in his writings, he drew important conclusions regarding the differences in the stress-optical behavior of glasses and crystals. He is credited by Coker and Filon (10) as being the first to measure the effect in diamond.

Pockels developed the original, universally accepted theory describing the stress-birefringence relation for all crystalline and non-crystalline forms of matter. The theory was published as his doctoral dissertation at Göttingen in 1889 (11). With minor corrections, Pockels' work is the basis for all investigations of the effect today. The theory was laid down in the compact notation now described as tensorial, so that a great amount of information was compressed into a few very brief equations. This theory is discussed in the next section.

Bhagavantam in 1942 (12) noted that Pockels has erred in the tabulation of constants for several crystal classes, and Bhagavantam and his associates have confirmed the corrections experimentally. Other than the work of Bhagavantam, there have been no contributions to the geometrical theory for over 60 years. Coker and Filon (10), Mason (13), and others have repeated the errors made by Pockels.

Explanations of the physical mechanism responsible for the stress birefringence are unsatisfactory when any quantitative predictions of the effect are made. Much of the work has been based upon inference from relations not involving pressure effects. The semi-classical work of Mueller (14) is the most comprehensive attempt; it gives a reasonable prediction of the magnitude of the effect, but fails to predict the positive or negative character. Burstein and Smith (15, 16) have more recently added some pertinent speculations on the behavior of the constituent particles in the stressed crystal, but the number of crystals studied is too small to test even the qualitative aspect of their hypothesis. The assumptions necessary to simplify any inclusive analysis of the problem will demand even more observations for their justification.

The number of crystals which have been studied quantitatively is about twenty. Wertheim observed four (9), Pockels seven; Ramachandran (17, 18) and his associates another seven or eight; and West, Makas (19, 20) and Burstein, Smith a few more. Several other crystals were studied qualitatively by Brewster and some lesser investigators of the nineteenth century. Ramachandran also measured the stress-birefringence effect in diamond; his work on this crystal is the only extensive work other than that of the present study. Until the present study, all measurements have been made at relatively low stresses. No previous studies have been made on crystals to determine the dispersion of the stress-optical constants with the wavelength of the light.

The infrared stress-optical effect has recently been studied by Bond

(21) and others interested in the properties of silicon and germanium. No published results are yet available on this work.

The stress-optical effect is commonly termed *photoelasticity* by members of the engineering profession. This term is not properly descriptive of the phenomenon. It is correct in that it implies a sort of optical strain arising from the application of stress; it does not, however, convey any idea of the manner in which the strain reveals itself. The necessity has arisen on several occasions to explain the meaning of *photoelasticity* to investigators completely familiar with many other vectorial properties of crystals. As a result of these considerations, the term *piezobirefringence* is suggested as a name for the birefringence produced by stress. This term describes in itself the nature of the phenomenon. It is compounded of familiar terms and is compatible with the names of other crystal properties, for example, pyro- and piezoelectricity. *Piezobirefringence* will be used throughout this paper in preference to *photoelasticity*.

Piezobirefringence is potentially of considerable importance in the study of the solid state. Several properties of "perfect" crystals can never be measured directly because of the great sensitivity of the properties to minute quantities of imperfections, either chemical or physical. Piezobirefringence effects are not especially sensitive to these quantitatively minor flaws. The effect itself, however, is closely related to several of these types of flaws, which produce a local or a general distortion of the crystal. The phenomenon of piezobirefringence is most obviously of direct application to the study of a general, overall distortion. Most crystals, even the best synthetic ones, show birefringence which is not justified by the idealized internal structure of the crystal. The exact cause of this birefringence is usually not known. Silicon and synthetic corundum are important examples in which "anomalous" double refraction is common; diamond is a familiar natural example. Screw dislocations and twinning are possible explanations; then again, very little systematic research has been done on the problem.

The paucity and inconsistency of available information on piezobirefringence, and the potential value of quantitative results inspired the present study. In the paper by Slawson and Denning (22) in this issue, the application of piezobirefringence studies to an interpretation of double refraction in natural diamond is discussed. The synthesis of the diamond was announced only after the present study was well underway. It can only be supposed that someday the growth of diamond crystals, and imperfections and dislocations in them will be as common topics in industrial discussions as they are for silicon and germanium today. The piezobirefringence investigations should be of assistance in such problems.

THEORY OF PIEZOBIREFRINGENCE

Geometrical Theory

Pockels developed the first geometrical theory of piezobirefringence in a generalized treatment, applicable to crystals of all classes and homogeneous non-crystalline substances. Pockels' theory is analogous to the commonly accepted theories describing all other vectorial properties of crystals. Within the present boundaries of experiment, all evidence has supported the basic assumptions of his theory. Bhagavantam's corrections to the development of the theory for various crystal classes have been partially verified experimentally by Bhagavantam and Suryanarayana (24), and theoretically by Bond (21), Mason (23), and the writer. Pockels' approach is nonetheless fundamentally sound; as modified by the corrections noted above, it is the theory presented here (25).

A non-absorbing triclinic crystal may be characterized optically for any one wavelength of light by specification of six independent quantities called the polarization constants. We designate the principal refractive indices as follows: $\alpha_1 = 1/\alpha$, $\alpha_2 = 1/\beta$, $\alpha_3 = 1/\gamma$. We let α_{ij} represent the cosine of the angle between the j th principal optical direction and the i th coordinate axis of a reference Cartesian frame in the crystal. Then the polarization constants a_{ij} are defined by

$$(1) \quad a_{ij} = \sum_{k=1}^3 \alpha_{ik} \alpha_{jk} \alpha_k$$

Since $a_{ij} = a_{ji}$, there are in reality only six independent constants a_{ij} .

Pockels postulated that stress is related to the change in optical properties by the equations

$$\Delta a_{ij} = a_{ij} - a_{ij}^0 = q_{ijkl} T_{kl},$$

where a_{ij} are the polarization constants in the stressed crystal, and a_{ij}^0 in the unstressed. The quantities q_{ijkl} compose the stress-optical tensor. A similar set of relations hold for strain; the corresponding quantities p_{ijkl} compose the strain-optical tensor.

In a three-dimensional space the expression q_{ijkl} comprises 81 possible independent quantities. The symmetry of the crystal class in question reduces the number of independent components. In the usual method of approach, the effects upon q_{ijkl} of a transformation of coordinates in accord with crystallographic laws of transformation are compared with the effects in accord with mathematical laws. It will then be found that in order to satisfy both theorems of transformation, certain linear relations must be satisfied by some q 's, while others must necessarily vanish. The reduction will be illustrated here for the five cubic classes.

The components q'_{ijkl} of a fourth order tensor in one set of rectangular

Cartesian coordinates are mathematically related to the components of the same tensor in another set by the equations

$$(2) \quad q'_{ijkl} = \frac{\partial x_i'}{\partial x_r} \frac{\partial x_j'}{\partial x_s} \frac{\partial x_k'}{\partial x_t} \frac{\partial x_l'}{\partial x_u} q_{rstu}.$$

The crystallographic transformation laws depend, of course, upon the symmetry of the crystal class. Class 23 will be considered first. The three-fold axis suggests a cyclic transformation in which we have $x_3' = x_2$, $x_2' = x_1$, and $x_1' = x_3$. Thus we see that

$$\frac{\partial x_i'}{\partial x_r} = +1 \text{ if } i = r + 1,$$

and

$$\frac{\partial x_i'}{\partial x_r} = 0 \text{ otherwise.}$$

Thus in equation (2) the only q'_{ijkl} which are not zero are those in which each primed subscript is one greater than each unprimed subscript. But crystallographic symmetry requires that $q'_{ijkl} = q_{ijkl}$. By induction, it follows that each q_{ijkl} is equal to the corresponding component with subscript increased by one, and hence by two. The number of independent components is thus reduced from 81 to 27.

The two-fold axis suggests the transformation $x_1' = -x_1$, $x_2' = -x_2$, $x_3' = x_3$. Thus we have

$$\frac{\partial x_i'}{\partial x_r} = -1 \text{ for } i = r = 1 \text{ or } 2.$$

$$\frac{\partial x_i'}{\partial x_r} = +1 \text{ for } i = r = 3,$$

$$\frac{\partial x_i'}{\partial x_r} = 0 \text{ otherwise.}$$

It is seen that in the mathematical transformation of q_{rstu} , equation (2), only one term remains on the right side, that in which the primed subscripts equal the unprimed. Hence we have $q'_{ijkl} = \pm q_{ijkl}$, depending on the values of the subscripts. If an even number of $(ijkl)$ have a value of 3, then we have $q'_{ijkl} = +q_{ijkl}$; if an odd number have a value of 3, then we have $q'_{ijkl} = -q_{ijkl}$. But crystal symmetry requires that $q'_{ijkl} = q_{ijkl}$. Therefore, q_{ijkl} vanishes for the odd case. The threefold axis requires that this result be valid for any other transformation of the same type. Hence the only non-zero components of the earlier 27 are those in which the subscripts occur in pairs. The independent components of the stress-optical tensor remaining at this stage are thus q_{1111} , q_{1122} , q_{1133} , q_{1212} , q_{2121} , q_{1221} , q_{2112} .

It will be remembered that in equation (1), both Δa_{ij} and T_{kl} are symmetric, that is, $\Delta a_{ij} = \Delta a_{ji}$ and $T_{kl} = T_{lk}$. There is thus seen to be no loss

in generality in taking $q_{ijkl} = q_{jikl}$ and $q_{ijkl} = q_{ijlk}$. The seven independent components are thus reduced to four, q_{1111} , q_{1122} , q_{1133} , q_{1212} . These are the stress-optical constants of class 23.

Class 23 is of considerably interest, since it is one of those for which Pockels was in error. Pockels deduced that there should be three independent stress-optical constants for each class in the cubic system. The result above is the first independent confirmation of Bhagavantam's group-theory proof of Pockels' error. Both Bond (21) and Mason (23) have indicated agreement with these more recent results.

The remaining cubic classes will be examined briefly. The next more symmetrical class after 23 is $m\bar{3}$. The axial planes suggest a transformation $x_1' = -x_1$, $x_2' = x_2$, $x_3' = x_3$. The transformation affords no relations between terms of differing subscripts; and since the non-zero partial derivatives are either $+1$ or -1 , and the four q_{ijkl} remaining have subscripts only in pairs, no conflict arises between mathematical and crystallographic transformation. The center corresponds to a transformation $x_i' = -x_i$, and by the same reasoning as above affords no reductions in the number of constants. Hence the scheme of independent constants for class $m\bar{3}$ is the same as for class 23.

In class $\bar{4}3m$, the diagonal planes make the crystal axes completely equivalent, as compared to their cyclical equivalence in classes 23 and $m\bar{3}$. In this case the formal transformation is $x_1' = x_1$, $x_2' = x_3$, $x_3' = x_2$. Both the crystallographic and mathematical transformations lead to the same results, $q_{1122} = q_{1133}$. This is the sole effect of the diagonal planes. The independent constants for class $\bar{4}3m$ are then q_{1111} , q_{1122} , q_{1212} .

In class 432, the four-fold axes have the same effect as the diagonal planes; equivalence of crystal axes. The formal transformation is $x_2' = x_3$, $x_3' = -x_2$, $x_1' = x_1$. This leads to the relation $q_{1122} = q_{1133}$. Crystallographic symmetry yields the same result. The independent stress-optical constants remain as q_{1111} , q_{1122} , q_{1212} .

In class $m\bar{3}m$, to which diamond belongs, the problem is not so much to see what effect the symmetry does have, but rather what it does not have. Complete axial equivalence yields $q_{1122} = q_{1133}$. As is evident by this time, the only transformations of value in the cubic system are those in which the derivatives are either ± 1 or 0. Such transformations make components vanish only if the subscripts do not occur in pairs. Such transformations bring about relations only between components having the same subscript pattern, for example, q_{aaab} and q_{jjjk} . In the three remaining stress-optical constants, all the subscripts occur in pairs, and none of the sets of subscripts follows the same pattern. Hence the independent constants for diamond, and all crystals of class $m\bar{3}m$, are q_{1111} , q_{1122} , q_{1212} .

The results for the various cubic classes are summarized in Table 1.

TABLE 1. STRESS-OPTICAL CONSTANTS OF CUBIC CRYSTALS

Class	Independent Components of Stress-optical Tensor	
	Pockels	Bhagavantam, Poindexter
23, $m\bar{3}$	$q_{1111}, q_{1122}, q_{1212}$	$q_{1111}, q_{1122}, q_{1135}, q_{1212}$
$\bar{4}3m, 432, m\bar{3}m$	$q_{1111}, q_{1122}, q_{1212}$	$q_{1111}, q_{1122}, q_{1212}$

It should be noted here that the constant q_{1111} relates a compression on the (100) face to the change in index of refraction for light polarized perpendicular to that face. The constant q_{1122} relates the same compression to the change in index for light polarized perpendicular to any (0kl) face. The constant q_{1212} relates a shear stress to the orientation of the indicatrix in the stressed crystal.

In the present study, the stress birefringence was measured, not the absolute change in index of refraction. Only two constants are required to characterize completely the birefringence effect in class $m\bar{3}m$. Exact expressions relating the stress to the resultant change in optical properties are given in a later section.

The stress-optical equations may be solved to give quantitative results, and thus prediction of the optical effect of any stress whatever. It is worthwhile, however, to examine qualitatively the behavior of cubic crystals under a single linear compression. Several simple rules serve to predict the nature of the change in optical properties produced by this stress. No justification other than intuition will be offered here for these rules; all can be rigorously verified by computation.

1. Any symmetry axis in the unstressed crystal which coincides with the axis of compression is also present in the stressed crystal.
2. A two- or four-fold axis normal to the axis of compression is present as a two-fold axis in the stressed crystal.
3. Symmetry planes parallel or normal to the compression axis are unaffected by the stress.
4. A center of symmetry is unaffected by the stress.
5. Any symmetry element not oriented as discussed above is destroyed by the compression.
6. No symmetry elements are created by the compression.

In accord with the above rules, it is seen that a single compression applied to an opposite pair of cube faces of crystals of classes 23 and $m\bar{3}$ produces in effect orthorhombic crystals of classes 222 and mmm , respectively. A similar stress in classes $\bar{4}3m, 432$, and $m\bar{3}m$ produces tetragonal

symmetry of classes $\bar{4}2m$, 42 , and $4/mmm$. Compression on an octahedron in any class converts the crystal to class 3 hexagonal. Compression in a general direction converts classes 23 , $\bar{4}3m$, and 43 into class 1 triclinic, and classes $m\bar{3}$ and $m3m$ into class $\bar{1}$ triclinic. The modified optical properties correspond, of course, to the modified symmetry of the stressed crystal.

The above rules can be of very real value in selecting the orientation of the crystal to be studied. It is impossible to measure all of the stress-optical constants by a single compression on a cube face; in fact, it is often inconvenient to measure any of them in this manner. A crystal with an easy octahedral cleavage, for example, may split too easily when stressed on the cube face. Furthermore, many substances have naturally occurring faces (or cleavages), not normal to the crystallographic axes, which are desirably left on the crystal specimen as reference planes. It turns out that all the stress-optical or stress-birefringence constants may be measured by simple compressions if the orientation of the specimen is properly chosen.

When a crystal is compressed on any but a cube face, it is necessary to derive stress-optical constants appropriate to the orientation. This procedure is far simpler than an attempt to resolve a general compression into its components along the crystal axes, and to relate these many components to the optical effect. The appropriate derived constants are related to the original constants by the theorem of tensor transformation, equation (2). The procedure will not be illustrated in this paper, but the derived constants for the orientations employed are given in the section on measured results.

PHYSICAL THEORY

The various physical theories of piezobirefringence have had only a very limited success in the correlation of prediction and experiment. All of the theories have required considerable amounts of data from other sources, often questionable in themselves, in order to translate symbols into measurable predictions. The theoretical work has been hindered by the lack of data on the piezobirefringent behavior of crystals. About twenty crystals have been studied, and they make up a rather heterogeneous lot as far as their stress-optical effects are concerned. It is necessary to postulate different mechanisms for each crystal to explain the observed effects. The most successful attacks have been semi-classical in nature; the quantum-mechanical approaches have been too complicated to permit of any predictions whatever.

The present investigation has included only a brief treatment of the problems of physical theory. Accordingly, only a short discussion of the

factors involved and a short résumé of the principal studies will be presented here.

We consider the crystal as a system of electric charges. When a charge system is subjected to an electrostatic field (it is assumed that magnetic fields have negligible interaction with the crystals concerned here), the energy E put into the charge system is related to the field strength F by the formula $E = -\frac{1}{2}\alpha F^2$. The quantity α is a constant for the system and is called the polarizability. The refractive index is theoretically related to the polarizability by the Lorentz-Lorenz equation,

$$\frac{n^2 - 1}{n^2 + 2} = \frac{4\pi}{3} \frac{L\alpha\rho}{M},$$

where M is molecular weight, L Avogadro's number, and ρ density. The total polarizability of a crystal is the resultant of three contributions: the electronic component, which arises from the distortion of the electron field around each nucleus; the ionic component, which arises from the movement of oppositely charged ions with respect to each other; and the orientational component, which arises from the rotation of dipolar molecules in certain types of crystals. In the optical range of frequencies, the inertia of ions and molecules prevents any appreciable movement; so the polarizability is almost entirely due to the deformation of the electronic orbits.

The effect of an applied electric field on any one particle in an assemblage of particles, such as a crystal, is modified by the reaction of the other particles. The total displacement of charge under the influence of the external field creates a counter-field in opposition to the applied field, which reduces the effectiveness of the applied field.

A more complete discussion of dielectric phenomena and mechanisms may be found in any text on crystal or solid-state physics.

Attempts to calculate the index of refraction for crystals have not been notably successful, despite the great amount of experimental data available. Empirical formulas can be found which fit certain groups of crystals better than the Lorentz-Lorenz equation, but none presents any striking improvement. The attempts to explain piezobirefringence have been even less successful. Banerjee (28) considered two effects. The first is the modification of the counter-field by the deformation of the crystal; the second is the effect of distortion of the constituent ions in the crystal. Mueller (14) observed, however, that Banerjee made a serious error in his choice of method for adding up the reactions of the particles in the crystal. Banerjee's predictions were compared with the observed behavior of only two substances, NaCl and KCl. Banerjee found acceptable results for these two; so another error, which compensates for the first,

is present. Banerjee did not attempt to apply his theory to other substances.

Herzfeld (29) and Herzfeld, Lee (30) considered the effect of the crystal deformation on the counter-field, and also considered the resultant modification of the electronic energy levels. The effect on the energy levels, which in turn determine the polarizability, was calculated by a second-order perturbation treatment commonly used in quantum mechanics. A distortion of the potential well around the nucleus was postulated as the perturbation. The method is sound, but Herzfeld concluded that the final equations require too many assumptions regarding the proper values of constants. Furthermore, Mueller pointed out several errors in computation; Herzfeld himself later admitted these.

Mueller (14) included in his calculations the effect of deformation on the counter-field, the effect on inter-ion spacing and the effect on the shape of the ions themselves. Mueller made no final calculations for covalent crystals; he did, however, by proper assumptions make the equations match the behavior of NaCl and KCl. The most unsatisfactory aspect of the theory is its inability to predict whether the refractive index increases or decreases under the effects of compression. His theory is the most complete of any on the topic, and Mueller concluded that it is satisfactory because it is at least not in opposition to the facts.

The extreme difficulties involved are well illustrated by the simplified quantum-mechanical treatment of the problem attempted in the present work. The Lorentz-Lorenz equation may be rearranged and differentiated to give

$$\frac{\partial n^2}{\partial \rho} = - \frac{4\pi L\alpha}{M \left(1 - \frac{4\pi L\alpha\rho}{3M}\right)^2}.$$

Since for any real value of n , the quantity $4\pi L\alpha\rho/3M$ must be less than 1, it is seen that an increase in density ρ causes an increase in refractive index. This direct effect is, of course, modified by the change in the nature of the counter-field under the deformation. The counter-field in turn depends not only on the directional alteration of the lattice constant, but upon the directional change in polarizability of the electron systems in the crystal. As far as optical properties are concerned, the density change is a bulk effect for either hydrostatic force or a single linear compression, and thus can produce no anisotropy. Piezobirefringence for any type of stress must be analyzed in terms of the anisotropies of the structure change and the polarizability. For hydrostatic compression, the density change, the modification of the structure, and the change in polarizability all affect the overall index change; but wheth-

er the crystal acquires greater or lesser birefringence again depends solely upon the latter two factors. The effects of polarizability change do not necessarily add to the direct effect of density change; there is some evidence at the present time that the refractive indices of some crystals decrease under hydrostatic pressure.

If we assume a simple one-electron "covalent" bond in a diamond-like crystal, the polarizability of the electron is given by (31)

$$\alpha = \frac{\left(\iiint_{-\infty}^{+\infty} \phi^2 z^2 dx dy dz \right)^2}{\iiint_{-\infty}^{+\infty} \phi z \frac{\partial \phi}{\partial z} dx dy dz} \frac{8\pi^2 m e^2}{h^2},$$

where ϕ is the appropriate wave function and z is the coordinate in the direction of the applied field. The function ϕ will vary with change in lattice constant; thus the polarizability will be changed. The expression, itself an approximation, would be extremely difficult to evaluate with exactness. The inclusion of the effects of the other charged particles in the crystal increases the difficulties still more. Under a single compression, some bonds will be lengthened, others shortened; bond angles will be changed. The change in polarizability will vary with direction. There is no obvious evidence that the effect of three equal linear compressions at right angles (hydrostatic force) is simply the sum effect of the three compressions applied individually. If such is not the case, Pockels' tensor treatment is incorrect. At the present time the experimental evidence is not sufficiently accurate to enable any conclusions on the latter possibility. In brief, expressions such as the one above are all but useless in a discussion of piezobirefringence.

Further elaboration of the physical theory would be futile at the present stage of understanding of the problem. Qualitative observations on the application of theory to the present work will be presented in a later section.

MEASUREMENT APPARATUS AND PROCEDURE

An interference method of observation was chosen for the present study. The principle may be used in measurements either of the piezobirefringence directly, or of the absolute change in refractive indices. In the first case, the specimen is stressed while in the 45° position between crossed polars, and the change in relative retardation is observed. The birefringence is then computed in the usual way, and the stress-birefringence constants calculated. To measure the absolute index change, the retardation of light polarized in the principal optical directions must be observed. This may be accomplished by splitting an appropriately polarized light beam with a half-silvered mirror, sending half through

and half around the crystal specimen, and observing the interference arising upon recombinations of the two halves of the beam. Localized fringes arising between two surfaces of the crystal may also be employed if the faces are nearly perfectly parallel.

In the present work, only the birefringence was observed. The technique developed for the study entails one important modification, not used heretofore, which increases the precision of the observations. The measurement of retardation was supplanted by measurement of transmitted light intensity; instead of an optical compensator, an electronic

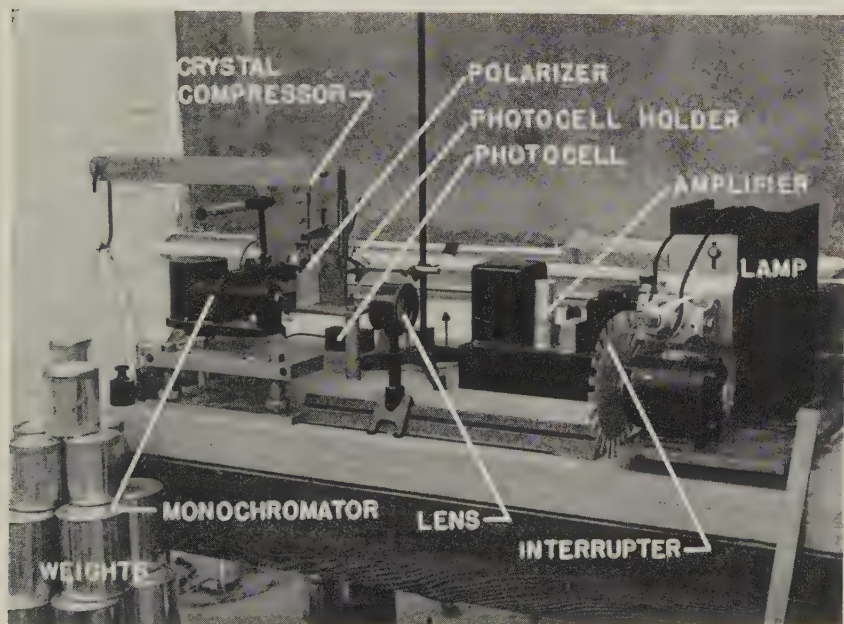


FIG. 1. Overall view of the measurement apparatus.

photometer was used. The advantages of this modification will be discussed shortly.

The measurement apparatus consists of a light source, 750-cps interrupter, monochromator, polarizer, crystal compressor, analyzer, photocell, and tuned amplifier, arranged in that sequence. A photograph of the apparatus is shown in Fig. 1. Note that the analyzer is not visible, and that the photocell is not in position in the clamp directly behind the compressor. Protective covers were removed from the device in order to reveal the component parts. An enlarged view of the compressor is shown in Fig. 2. Both polarizer and analyzer are moved from the light

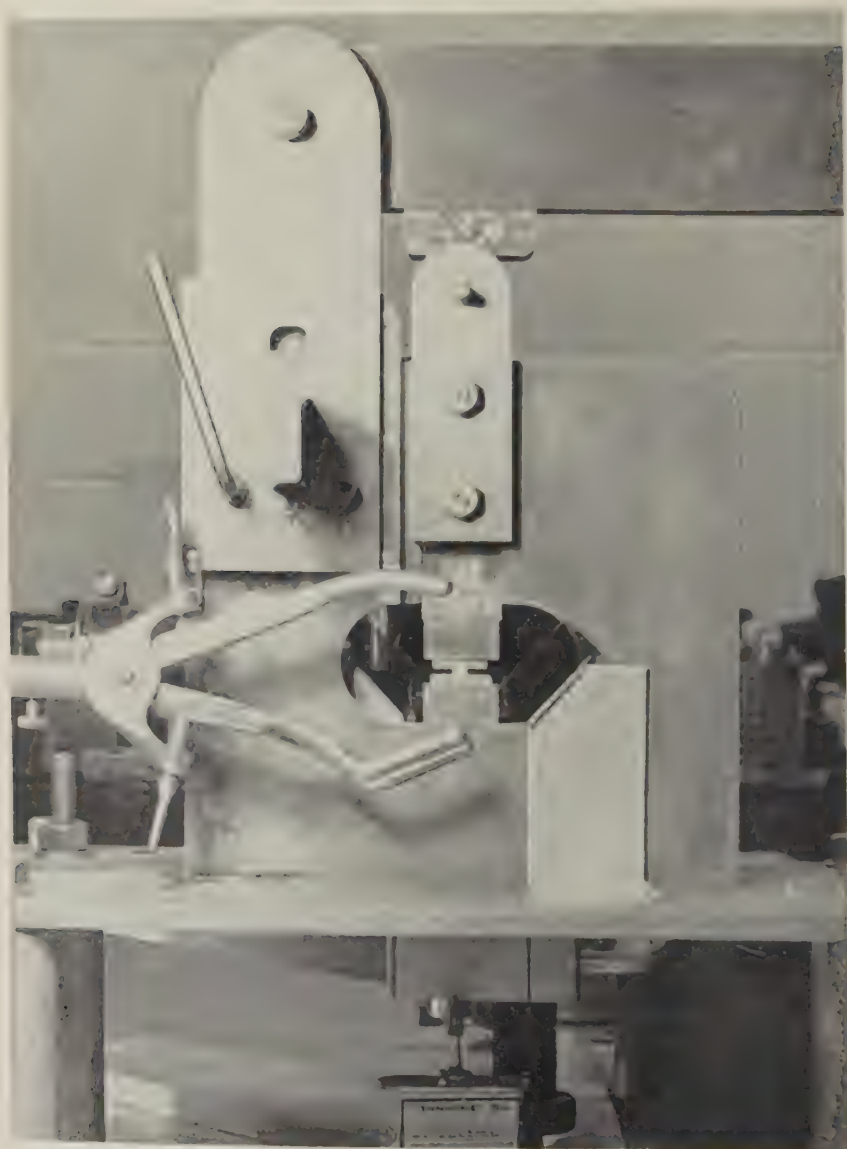


FIG. 2. The crystal compressor. The polaroids and photocell are not in position.
The crystal is mounted as in actual measurements.

path, and the photocell is out of sight. The crystal is mounted as in actual measurement, and it may be seen brightly illuminated by the beam from the monochromator directly behind.

The construction of the apparatus is almost self-explanatory from the illustrations, and will not be discussed.

MEASUREMENT TECHNIQUE

The technique employed in the present study requires that the crystal specimen be shaped in the form of a parallelepiped, roughly equidimensional. The specimen is placed between crossed polars, which are in the 45° position, and subjected to a single linear compression on one pair of faces normal to the polars. The relative retardation produced by a known stress is observed. The piezobirefringence constants may then be computed from relations derived later.

The present study initiated a modified method of observing the retardation which has several important advantages. The first difference between the new and the old is that the apparatus measures only the relative intensity of the transmitted light; it is not well adapted for direct measurement of retardation. The second difference is that the crystal is examined over the entire visible area of one face, rather than in selected small regions. The second difference is in one respect a consequence of the first, and it greatly facilitates accurate measurement. In the older method, the results of observation at several points on the crystal face were averaged. This method can present serious difficulties, because of the non-uniformity of the stress distribution in the crystal. In the present method, the observed quantity is light intensity; it is easily possible to obtain an integrated average over the face of the crystal by placing the photocell so that all of the transmitted light is intercepted. There is no way to measure the average retardation directly with such facility. This automatic average is the most significant improvement afforded by the intensity method of observation.

The observation procedure is such as to reduce the effects of instrumental failings and observational misjudgments. Though the instrument was designed to measure intensity of light, only the successive maxima and minima of transmission under increasing stress were recorded. Thus the transfer characteristic of the amplifier has no influence whatever upon the results. The accuracy of the photometric determination of retardation is about as good as that obtainable with a Babinet compensator, that is, about $1/400$ wavelength (32).

Obtaining a uniform stress distribution in the crystal is a very critical consideration. The observations were in effect averages over an entire crystal face. Nevertheless, the observed quantity, light intensity, is related to the stress in such a way that any non-uniformity of stress distribution is reflected as an increase in the apparent values of the piezobirefringence constants. It is desirable that the maximum variation in stress not exceed $\pm 20\%$. In such a case, the correction is no greater than 1% , which can be applied with confidence. If the non-uniformity exceeds $\pm 20\%$, the correction increases very rapidly, and soon becomes so sensitive to the distribution as to be useless in application.

Although $\pm 20\%$ may appear a generous tolerance, attainment of such a degree of uniformity is a matter of some difficulty. Simple pads of resilient material inserted between crystal and compressor jaws were not adequate. Rubber and lead tended to spread laterally from beneath the crystal, with the result that the stress was very much higher in the center of the crystal. Cardboard became very compact after a few compressions and thereby lost its value as a pad. Celluloid performed very well, but internal rearrangement in the material destroyed its effectiveness very rapidly. Furthermore, the shape and size of simple pads of any material is so critical that the ideal form is seldom obtained. These difficulties led to abandonment of the simple pad.

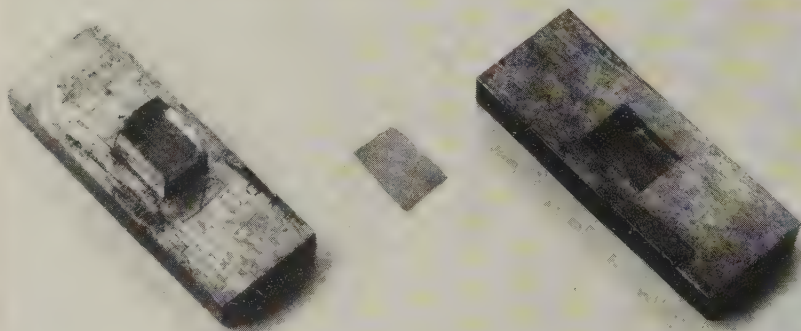


FIG. 3. View of crystal mounting pads. In order from left to right are a pad with the diamond in place, a dental rubber cushion, and the other pad. The rubber is to be placed in the bottom of the well of the empty pad before insertion of the crystal.

A semi-hydrostatic crystal mount was the eventual solution to the problem. Small brass blocks were made which receive the crystal snugly in rectangular wells. A thin layer of soft solder was placed in the bottom of the wells. Under any compression of greater than about 9000 psi, the solder behaves as a viscous fluid and distributes the load evenly over the face of the crystal. To improve the performance below the yield point of solder, an additional pad of dental dam rubber was inserted between the crystal and the solder layer. An enlarged view of the compound pads is shown in Fig. 3.

The performance of the compound pads has been very satisfactory. The effective variation in stress was typically $\pm 15\%$, and at very high stresses, often no worse than $\pm 2\%$.

The range of stresses throughout which measurements were made serves as a valuable check on the performance of the pads and the ac-

curacy of the observations. Previous piezobirefringence studies were limited to stresses of the order of 100 kg/cm.² In the present work, pressures were carried to a maximum of 3000 kg/cm.² The observed linearity of the piezobirefringence effect to these high stresses is very good evidence that the measurement technique is satisfactory.

ERRORS AND CORRECTIONS

Three predictable sources of error are present in the measurement process. The first is the non-uniformity of stress distribution in the crystal; the second is the joint effect of the pass-band of the monochromator, the spectral emission curve of the lamp, and the spectral response of the phototubes; the third is the divergence of the light beam passed through the crystal. These three faults cause errors which can be computed to within $\pm 20\%$ of their own true value; so in each case a small correction is applied to the data.

The first source of error is the non-uniformity of stress distribution. It should be noted that variations in stress along any ray of light through the crystal can cause no error as long as the stress-retardation effect is linear. The observed intensity is a function of the total retardation along the path of the ray, regardless of the history of the ray. Variation in total retardation in a direction normal to the ray, however, does produce an error in the measurement. Such variation results in variation in the intensity of the light reaching the photocell from various portions of the crystal. The observed readings may be corrected if the approximate degree of the non-uniformity is known.

If the effective stress non-uniformity is $1 \pm p$ times the mean stress, then it can easily be shown that the stress producing an observed minimum in light transmission is $T = T^0 / 1 + p^2$, where T^0 is the stress producing a minimum if the stress were uniform. The degree of non-uniformity may be noted by scanning the face of the crystal with a narrow slit. The transmission I at a minimum may also be shown to be related to the non-uniformity by the expression

$$T = \frac{T^0}{1 + \frac{2I}{\pi^2}}.$$

Both methods were used as a check on the value of the correction. It is seen that a value for p of 0.1, corresponding to a total variation in stress of about $\pm 20\%$, gives rise to a correction of 1%.

The combination of tungsten radiator and phototube produced virtual sensitivity peaks in the green and infrared. The monochromator was set to have a pass band with half-intensity points 100Å apart. Thus the effective wavelength was not exactly that indicated on the monochroma-

tor scale. This error was evaluated approximately; it was found that the greatest correction to the piezobirefringence constants is 0.15%. This is so small that it is hardly worth consideration.

The light was not collimated before passing through the crystal. The divergence is approximately 1.3° in the diamond. This results in an increase in effective path length in the crystal of about 0.07%, again hardly worthy of notice.

Several unpredictable sources of error were observed. These were friction in the compressor, inaccuracies in the loading weights, rapid shifts in line voltage, and non-uniformity of the phototube cathode surface. No attempt was made to correct for any of these.

RESULTS AND CONCLUSIONS

In the section on theory it was shown that the diamond requires three constants to enable complete description of the optical effect produced by a general stress. These three constants, the stress-optical constants, are designated as q_{1111} , q_{1122} , q_{1212} . The physical interpretation of these constants should be reviewed at this time. The constant q_{1111} relates the compression on a pair of crystallographic cube faces to the change in refractive index for light whose vibration direction is normal to those faces. The constant q_{1122} relates the same stress to the change in index for light whose vibration direction is parallel to those faces. The constant q_{1212} relates a shear stress to the orientation of the resultant indicatrix.

In the present study, the birefringence was investigated, not the absolute change in index of refraction. Since birefringence is a difference in indices, fewer constants are needed to specify the birefringence effect. For compression on a cube, the birefringence is related to the stress by the constant $q_{1111} - q_{1122}$. The constant q_{1212} has, of course, the same significance as before. These two constants have been called the piezobirefringence constants in previous sections.

The piezobirefringence constants may be measured conveniently with a rectangular parallelepiped of a single crystal of the substance. If both constants are to be measured, the orientation of the parallelepiped must not coincide with a crystallographic cube. For diamond, a suitable form is bounded by the (111), $(1\bar{1}0)$, and $(11\bar{2})$ faces. The specimen used in the present study was prepared in that form.

The diamond parallelepiped was cut from an octahedron of exceptional quality. The uncut crystal weighed 3.6 carats. The natural (111) faces were left on the crystal untouched, since they were very smooth and flat. Artificial $(1\bar{1}0)$ and $(11\bar{2})$ faces were ground and given an optical polish. The orientations of the artificial faces were held to within $10'$ of the theoretical position by frequent checks on an optical goniometer during the cutting. The finished specimen is 3.31mm by 3.91mm by

4.57mm and weighs slightly over one carat. The largest face is the dodecahedron and the smallest the octahedron. The crystal is colorless, and unusually free of inherent double refraction, flaws, and twinning. The crystal appears "perfect" under 100 \times magnification.

The choice of orientation enables both piezobirefringence constants to be measured by stressing the crystal on the different faces. The piezobirefringence effect is most conveniently described by secondary constants, derived from the two constants given earlier, and appropriate to the orientation of the crystal. The computation of these constants will not be given here; the secondary constants are related to the original two by the law of tensor transformation. The constants for the orientations employed in the present study are given in Table 2.

TABLE 2. PIEZOBIREFRINGENCE CONSTANTS FOR VARIOUS ORIENTATIONS

Direction of Compression	Direction of Observation	Piezobirefringence Constant, Q
[111]	[112] or [1 $\bar{1}$ 0]	$2q_{1212}$
[112]	[111]	$\frac{1}{3}(q_{1111} - q_{1122} + 4q_{1212})$
[112]	[1 $\bar{1}$ 0]	$\frac{1}{6}\sqrt{9(q_{1111} - q_{1122})^2 - 6(q_{1111} - q_{1122})(2q_{1212}) + 33(2q_{1212})^2}$

The piezobirefringence constant is related to the observed retardation R and the stress T by the equation

$$Q = \frac{2\lambda R}{dn_0^3 T},$$

where Q represents the appropriate constant, selected from the table, and d is optical path length.

MEASURED RESULTS

Both primary piezobirefringence constants were measured for only one wavelength, 5400 Å. The sensitivity of the apparatus is greatest at this wavelength. Furthermore, this wavelength is approximately the average of the wavelengths employed by other investigators. The values recorded for $2q_{1212}$ were obtained by inspection of the trend of observed results in the neighborhood of 5400 Å. The values for the other constants are the averages of eight measurements at 5400 Å. These results are shown in Table 3.

The significant fact to be drawn from the results of the present study is the very slight deviation from piezobirefringent isotropy. Wertheim (10) made the first determination of the piezobirefringence constant for diamond in the early 1850's. He has been discredited by most later in-

TABLE 3. OBSERVED AND COMPUTED VALUES OF PIEZOBIREFRINGENCE CONSTANTS

Direction of Compression	Direction of Observation	Q	Average Value	Observed
[111]	[1 $\bar{1}$ 0]	$2q_{1212}$	2.97×10^{-14}	cm ² /dyne
[111]	[11 $\bar{2}$]	$2q_{1212}$	2.99	
(A) [11 $\bar{2}$]	[111]	$\frac{1}{3}(q_{1111} - q_{1122} + 4q_{1212})$	3.00	
(B) [11 $\bar{2}$]	[1 $\bar{1}$ 0]	(see Table 2)	3.01	
Computed Results				
[100]	[010]	$q_{1111} - q_{1122}$	3.04	from (A)
			3.07	from (B)

investigators because he reported only one value, and did not specify the orientation of the crystal studied. The results of the present study imply that there is no great need to specify orientation.

The measurements by the three principle investigators are summarized in Table 4.

TABLE 4. COMPARISON OF PIEZOBIREFRINGENCE MEASUREMENTS BY DIFFERENT INVESTIGATORS

Q	Wertheim c. 1850 (10)	Ramachandran		Poindexter 1955
		1947 (47)	1948 (18)	
$q_{1111} - q_{1122}$	3.3	7.8	7.2	3.04
$2q_{1212}$		2.6	2.7	2.98
$\frac{1}{3}(q_{1111} - q_{1122} + 4q_{1212})$			4.2	3.00

The factor 10^{-14} cm²/dyne has been omitted from all values.

Ramachandran's results show pronounced anisotropy.

The difference between his results and those of the other two studies is at first inspection suggestive of gross errors in technique or arithmetic. Ramachandran performed his measurements on specimens oriented the same as those used in the present study. For such specimens, the constant $2q_{1212}$ may be observed directly, but $q_{1111} - q_{1122}$ must be computed from a relation which tends to magnify errors in the values of the observed data. Ramachandran used simple pads of lead to distribute the stress on the crystal. It was found in the present study that such pads do not distribute the stress satisfactorily. Furthermore, Ramachandran did not carry his stresses to much beyond 100 kg/cm², which does not produce even $\frac{1}{2}$ wavelength of retardation. In view of these facts, his observed results for two of the Q 's are not unreasonable; the value derived from these, $q_{1111} - q_{1122}$, is necessarily far more inaccurate.

There are several arguments favoring near-isotropy of the piezobirefringence effect in diamond. If it is assumed that the birefringence is in reality a strain-dependent phenomenon, then the elastic and piezobirefringence effects should be analogous. A comparison of the two properties for several cubic crystals is shown in Table 5. It is seen that in general,

TABLE 5. CRYSTAL ELASTICITY AND PIEZOBIREFRINGENCE PROPERTIES

Crystal	Compliance		Ref.	Piezobiref.		Ref.
	s_1	s_3		q_1	q_3	
Diamond	1.8	2.3	(26)	3.0	3.0	—
NaCl	29	78	(26)	12	8	(25)
LiF	13.6	15.9	(32)	14	7	(19)
MgO	4.9	6.4	(32)	12	6	(19)
CaF ₂	8.4	29.6	(32)	14	-7	(25)
KBr	36	161	(32)	-16	47	(19)
KCl	28	156	(32)	-17	42	(25)

The abbreviated symbols designate the following constants:

$$s_1 = s_{1111} - s_{1122}, s_3 = 2s_{1212}, q_1 = q_{1111} - q_{1122}, q_3 = 2q_{1212}.$$

The units for the compliance constants are $10^{-13}\text{cm}^2/\text{dyne}$; for the piezobirefringence constants $10^{-14}\text{cm}^2/\text{dyne}$.

crystals showing greater elastic anisotropy also show greater piezobirefringent anisotropy.

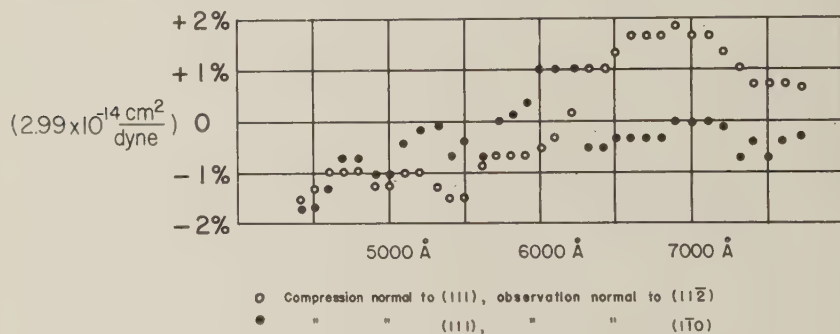
Another argument favoring near-isotropy for diamond may be based on the internal structure of the crystals. In the case of ionic crystals, the atoms are effectively in contact. A distortion of the crystal structure produces a distortion of the electron shells of these ions, which in turn causes a considerable directional difference in polarizability of the ions. It is easily visualized how the nature of the ion distortion will vary with the direction of the applied compression. In KBr, for example, which has the halite structure, a compression on (100) forces the ions directly against each other. A compression on (111), however, tends to force the ions between neighboring ions. The nature of the distortion introduced and the resultant effect on polarizability of the ions is thus markedly different for different directions of stress.

In the case of diamond, an entirely different disposition of particles prevails. Individual ions are not in contact at all. The structure is essentially an array of very compact C^{+4} nuclei relatively widely separated, but bound by electrons which move around two adjacent nuclei. A distortion of the crystal does not affect the nuclei at all. Bond distances are altered, and bond angles changed. These changes bring about modifi-

cations of the polarizabilities of the bonding electrons. The sum of polarizabilities in one direction no longer equals the sum in another; so the crystal has become birefringent. Regardless of the direction of compression, the effect is much the same.

The near isotropy of the piezobirefringence effect in diamond has been observed by Slawson and Denning (23). The same isotropy has been predicted for silicon (which has the same structure as diamond) by Bond (21).

The values of the constant $2q_{1212}$ observed at various wavelengths are shown in Fig. 4. No dispersion of the constant can be deduced with certainty from the data. The variation is at most $\pm 1\%$ throughout the



Each point represents the average of four measurements

FIG. 4. Dependence of $2q_{1212}$ upon wavelength.

range of wavelengths studied. The limit of accuracy of the observations is of this order. It should be remembered that the retardation is proportional to the stress and the cube of the reciprocal of the refractive index. For diamond, the quantity n^3 is nearly 10% greater for light of wavelength 4400 Å than for light of 7700 Å. The first impression upon inspection of the observed data is that the piezobirefringence effect does vary substantially with wavelength. No theoretical explanation is currently available to justify either dispersion or non-dispersion of the property. The present work marks the first time the wavelength dependence of the piezobirefringence effect has been studied for any crystal.

The piezobirefringent behavior at increasing values of stress for several wavelengths is shown in the next series of graphs, Fig. 5. The plotted points are not averages in this case, but represent values observed with crystal mounts producing the most nearly uniform stress distribution at the higher stresses. This is the first time that the piezobirefringence of diamond, or any crystal, has been studied at such high stresses. Ramachandran employed pressures of about 100 kg/cm². The observed linearity of the stress-retardation effect to pressures of nearly 3000 kg/cm²

(40,000 psi) yields very valuable information. The combined effects of the pass band of the monochromator, the sensitivity curve of the lamp-phototube combination, and the non-uniformity of stress distribution become increasingly troublesome at higher stresses. The close agreement of measurements at both high and low stresses is very good evidence of the accuracy of the determinations.

No hysteresis or permanent deformation could be observed in the piezobirefringence of the diamond. The crystal was left stressed for

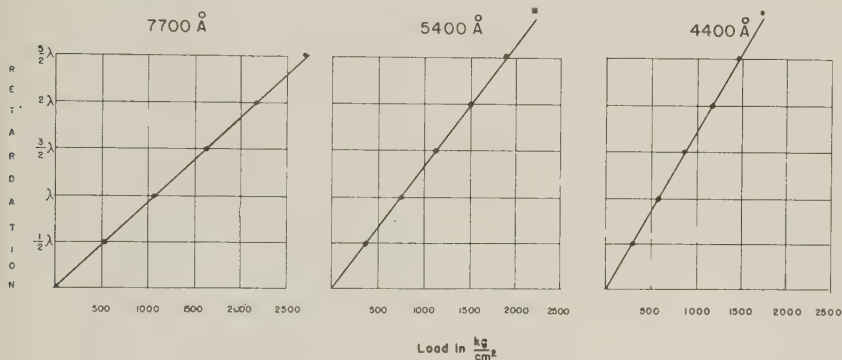


FIG. 5. Retardation versus applied load.

periods of up to one week at pressures of 30,000 psi. Upon removal of the load, a process requiring about a second, the transmitted light returned as fast as the millimeter could indicate to the original no-load value. The original diamond octahedron was stressed very non-uniformly between v-shaped jaws at maximum concentrated loads of 45,000 psi, and likewise showed neither hysteresis upon application or removal of load, nor permanent deformation under prolonged stress. This behavior is to be expected because of the very great structural strength of the diamond.

The diamond behaves as a negative uniaxial crystal when compressed on (100) or (111); the short axis of the indicatrix is parallel to the axis of compression. For compression in any other direction, the crystal becomes negative biaxial. This is deduced by noting that the index for light vibrating along the stress axis is always less than that for light polarized perpendicular to the stress axis, and that the indices for the perpendicular waves are nearly identical. In fact, the maximum difference in indices for light vibrating normal to the compression axis is so slight that the crystal is virtually uniaxial for any compression. The behavior of diamond in these respects for visible light is similar to the behavior of silicon in the near infrared (21).

ACKNOWLEDGMENTS

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PLEOCHROISM IN SYNTHETIC RUBY*

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ABSTRACT

A generally applicable method of quantitatively determining pleochroism of weakly absorbing crystals by the use of spheres is described. Sections of surfaces representing biabsorption ($K_e - K_o$ against wave normal are given. The use of biabsorption as an optical constant is suggested.

Pleochroism is a much neglected optical property of crystals. A few quantitative studies have been made on selected sections of certain crystals. Most of the published data have been obtained from selected plane crystal sections.

The earlier work on pleochroism was performed by European investigators. Babinet (1838) found that, with many exceptions, the greatest absorption in a crystal is along the direction of greatest refractive index. Laspeyres (1879-80) was the first to recognize the existence of "absorption axes," which he defined as the directions of greatest, least, and intermediate absorption in a crystal. He also found that an absorption surface in biaxial crystals is oriented, with respect to symmetry, in a manner similar to the orientation of the indicatrix, but that it does not necessarily coincide with the latter. Voigt (1885) supported this latter finding, as did Becquerel (1887). Ramsay (1887-88) in a study of cylinders and plates of epidote concluded that the absorption axes in plane (010) in monoclinic crystals were not mutually perpendicular. This implies that absorption is nonellipsoidal. Ehlers (1897-98) reported mutually perpendicular absorption axes, inclined with respect to the principal vibration directions, in certain monoclinic crystals. Johannsen (1916) shows absorption surfaces for three uniaxial substances without reference to the color of light used. He also gives a bibliography of the earlier work relating to the absorption of light in crystals. Slawson and Thibault (1939) quantitatively determined the pleochroism of a tourmaline crystal throughout the visible spectrum, for a propagation direction perpendicular to the optic axis.

Because of some uncertainty of the quantitative aspects of pleochroism, particularly whether it is an ellipsoidal property, and because of some ambiguity concerning the use of the terms absorption surface and absorption axes in weakly absorbing crystals (crystals that transmit

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appreciable light in fairly thick sections), a quantitative study was made of the pleochroism of synthetic ruby.

In order to develop easily a three dimensional surface a sphere made by Linde Air Products was used. Synthetic ruby was chosen for investigation because of the ease of obtaining such spheres.

Since pleochroism is the relative absorption with respect to direction, the absolute absorption need not be measured. The method employed consisted of measuring the relative intensity of light in two vibration directions associated with selected wave normals.

The ruby sphere (which was actually slightly biaxial) was mounted and carefully centered on a spindle so that it could be rotated about a normal to its c -axis. Selected monochromatic or nearly monochromatic light sources were used. The light source was imaged on the sphere. A lens focused an image of the illuminated sphere on a small adjustable slit. A Wollaston double image prism next to the slit served to produce separate adjacent images of the slit. This permitted the direct comparison of the ordinary and extraordinary light as in an ordinary dichroscope. These double images were examined by means of a microscope fitted with a rotating analyzing prism. Wave normals, rather than the slightly different ray directions, are more useful in such measurements, for while in general the extraordinary ray is deviated from the direction of perpendicularly incident light, the extraordinary wave normal is not. Since the incident light cannot be made perfectly parallel, and since the surface of the crystal used was spherical, the wave normals were not strictly parallel. The dimensions of the apparatus and the location and size of apertures were such that within the crystal the maximum angular deviation of wave normals from the desired direction did not exceed 6° . A schematic diagram of the apparatus is shown in Fig. 1.

For a particular wave length of light, and for given wave normal

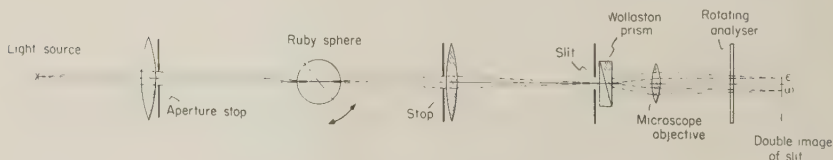


FIG. 1. Schematic diagram of apparatus.

directions in the crystal, the two adjacent slit images may be made of equal brightness by rotating the analyzer so that the line of demarcation between the two halves of the field practically disappears. If the angle through which the analyzer must be rotated from the extraordinary vibration direction of the ruby toward the ordinary is θ , then the in-

tensity ratio is

$$\frac{I_{\omega}}{I_{\epsilon'}} = \cot^2 \theta. \quad (1)$$

If I_0 is the intensity of the incident light, then the transmitted intensities are

$$I_{\omega} = I_0 e^{(-4\pi/\lambda_0)K_{\omega}t} \quad (2)$$

and

$$I_{\epsilon'} = I_0 e^{(-4\pi/\lambda_0)K_{\epsilon'}t} \quad (3)$$

for the ordinary and extraordinary vibrations respectively. K is the absorption coefficient (Berek, 1937), λ_0 the wave length in air and t the thickness.

Equations (2) and (3) may be combined as

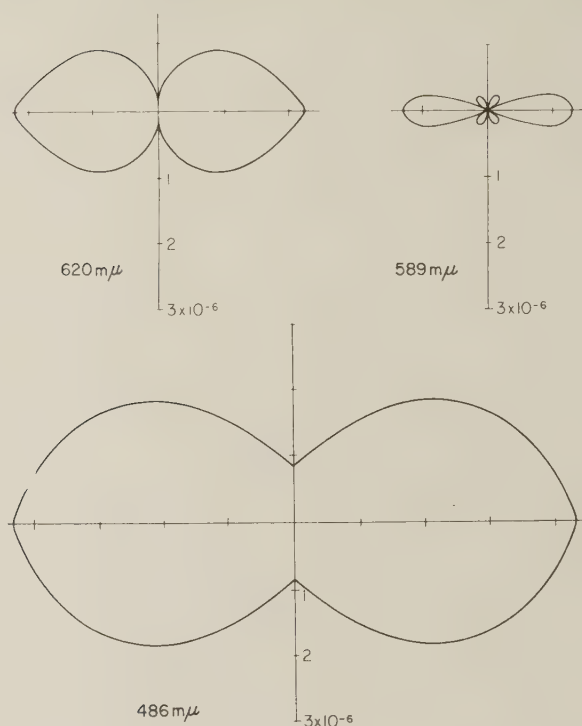
$$\frac{\lambda_0}{4\pi} \ln \left(\frac{I_{\omega}}{I_{\epsilon'}} \right) = t(K_{\epsilon'} - K_{\omega}). \quad (4)$$

Equation (4) is analogous to the well-known relationship between retardation, thickness and birefringence. For this reason it is proposed that $(K_{\epsilon'} - K_{\omega})$ be called biabsorption. Biabsorption, like birefringence, is dimensionless and is independent of the thickness of the crystal. Unless a particular wave normal direction is specified, the term biabsorption should refer to the maximum or principal value $(K_{\epsilon} - K_{\omega})$ as in the case of birefringence. The value for intermediate directions $(K_{\epsilon'} - K_{\omega})$ may lie between the maximum and zero. A surface useful in visualizing the quantitative aspects of pleochroism can be constructed by plotting biabsorption against wave normal direction for a particular wave length. The biabsorption for a given wave length in air and for a selected wave normal direction may be determined from the measured θ and t .

$$(K_{\epsilon'} - K_{\omega}) = \frac{\lambda_0 \ln \cot^2 \theta}{4\pi t}. \quad (5)$$

Several light sources were used to provide suitable approximately monochromatic light. A ribbon filament incandescent lamp was employed with a single layer interference filter to provide $486 \text{ m}\mu$, and with a Wratten A and wedge interference filter for $620 \text{ m}\mu$. An arc lamp and Wratten 87 filter furnished radiation of about $800 \text{ m}\mu$ which was observed with an infrared image converter tube. A sodium lamp supplied $589 \text{ m}\mu$ light. A mercury $546 \text{ m}\mu$ source could not be used because of the relatively strong absorption band of the synthetic ruby in that portion of the spectrum.

The diameter of the sphere used was 9.52 mm . For each wave length two settings were made for the θ values, after a few preliminary trials to

FIG. 2. Biabsorption curves for synthetic ruby, c -axis vertical.

gain experience in matching the two halves of the field. Such readings were obtained for successive wave normal directions which made an angle ρ with the c -axis of the crystal sphere. The results of the measure-

TABLE 1. (FOUR QUADRANTS AVERAGED)

ρ	486 mμ ($K_{\epsilon'} - K_{\omega}$)	σ	589 mμ ($K_{\epsilon'} - K_{\omega}$)	σ	620 mμ ($K_{\epsilon'} - K_{\omega}$)	σ
0	-0.86 $\times 10^{-6}$	0.2 $\times 10^{-6}$	-0.04 $\times 10^{-6}$	0.05 $\times 10^{-6}$	-0.07 $\times 10^{-6}$	0.1 $\times 10^{-6}$
10	-1.02	0.3	-0.17	0.1	-0.06	0.1
20	-1.32	0.3	-0.17	0.1	-0.11	0.2
30	-1.69	0.1	-0.24	0.1	-0.80	0.1
40	-2.25	0.2	-0.24	0.1	-1.13	0.2
50	-2.85	0.2	-0.20	0.1	-1.36	0.1
60	-3.37	0.2	0.00	0.1	-1.56	0.1
70	-3.77	0.2	+0.28	0.2	-1.75	0.1
80	-4.09	0.3	+1.17	0.4	-1.97	0.1
90	-4.32	0.3	+1.80	0.4	-2.27	0.1

ments of four quadrants were combined to yield the curves of Fig. 2. The average values of the absorption coefficients are tabulated in Table 1. The measurements were made in the plane of the optic axes.

For most of the data, eight measurements were averaged. The standard deviations were determined from the angular readings. The computed standard deviation, σ of each value of biabsorption, is also given.

An unexpected result of the measurements is the fact that the biabsorption for light of $486\text{ m}\mu$ parallel to the c -axis is not zero. Careful optical alignment, adjustment, and repetition of readings did not remove this apparent anomaly.

It may be that the actual biaxial nature of the crystal, probably the result of internal stress, may contribute to this condition. It must be admitted, however, that one would not expect such a condition to have so large an effect on the absorption coefficient. The curves for the other wave lengths of light do not show a significant departure of the biabsorption from zero for light propagated parallel to the c -axis.

The curve for sodium light shows weak pleochroism ($O > E$ or negative biabsorption) for values of ρ from 0 to 60° . The curve passes through zero at $\rho = 60^\circ$. From 60° to 90° the absorption scheme is reversed ($O < E$ or positive biabsorption). The change of sign of biabsorption cannot, in the authors' opinion, be attributed to experimental error. For yellow light travelling parallel to the c -axis, the biabsorption is practically zero (that is, there is no pleochroism exhibited) within experimental error.

For red light, about $620\text{ m}\mu$, the biabsorption is negative for all values. Along the c -axis the value is again practically zero.

In the near infra-red, approximately $800\text{ m}\mu$, the biabsorption is zero in the c -axis direction and is small (negative) for all other directions. The maximum observed value is -0.84×10^{-6} . The readings obtained were too widely scattered to justify plotting a curve. It was found difficult to match accurately the brightness of the two fields observed in the image converter (snooperscope) tube.

In a uniaxial substance, such as the ruby, the K_ω is independent of direction within the crystal. That this is true was demonstrated by comparing the intensity of the ordinary rays from the crystal with linearly polarized light passed around the crystal and into the Wollaston prism so that a setting of the analyzer could be made to balance the field.

For comparison Fig. 3 shows a curve of birefringence. The value of $(\epsilon' - \omega)$ is plotted for the assumed indices $\omega = 1.772$, $\epsilon = 1.763$. The well-known equation of this curve is $(\epsilon' - \omega) = (\epsilon - \omega) \sin^2 \rho$ which is very close to the more accurate relation

$$\left(\frac{1}{\omega^2} - \frac{1}{\epsilon'^2}\right) = \left(\frac{1}{\omega^2} - \frac{1}{\epsilon^2}\right) \sin^2 \rho.$$

When a suitable constant (ω) is added to the radius vectors of this curve an ellipse is produced (inverse to a meridian section of the indicatrix) which represents the variation of ϵ' with respect to wave normal direction.

If a similar constant (K_ω) is added to the biabsorption curves, then the curve which results represents the variation of K_ϵ' with respect to wave normal direction.

Since for most of the visible spectrum the absorption coefficient, K , for the ruby used is of the order of 5×10^{-5} (this value was not measured accurately) it is practical to consider the indicatrix as an ellipsoid. The complex index ($n-ik$), in which i is $\sqrt{-1}$, is practically equal to n .

Because of recent developments, the study of minor impurities of

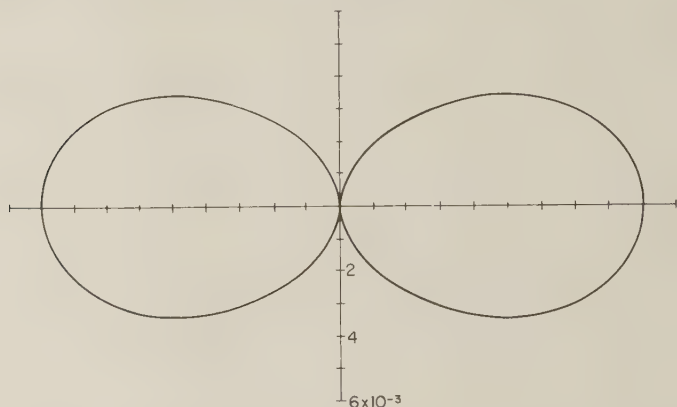


FIG. 3. Birefringence with respect to wave normal direction for synthetic ruby.
 c -axis vertical.

crystals has assumed increasingly greater importance. For this reason it is thought that for some series of weakly absorbing compounds biabsorption for a specified wave normal direction and for selected wave lengths might be a useful optical constant. The value of biabsorption could be determined from thin sections by methods analogous to those used for the determination of bireflection of strongly absorbing crystals.

The writers are indebted to the Linde Air Products Company, who furnished the synthetic ruby sphere for the investigation.

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CHALCHIHUITL—A STUDY IN JADE

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ABSTRACT

The Aztec gem stone *chalchihuitl* is jadeite, or its congeners diopside-jadeite and chloromelanite. The various categories of *chalchihuitl* recognized by the Aztecs are identified. Its occurrence with the serpentine rocks of Guatemala is suggested, and a natural occurrence in the Motagua Valley is recorded.

INTRODUCTION

When the Spanish explorers of the early 16th century reached the coast of Mexico, they found a bright green stone in use among the inhabitants of the region which the indigenous lapidaries fashioned into ornaments and figurines. The early chroniclers, impressed by the vivid green color of the stone and by the great value placed upon it by the natives, referred to it as emerald. This is not surprising since they had no previous experience with a stone of this nature, and the superior quality of the emeralds recovered as loot from the Incas of Peru, and later from the mines of Colombia, was not yet known to them.

The Aztecs of Mexico, who particularly esteemed this stone, and demanded it in tribute from their vassals, called it *chalchihuitl* (pl. *chalchiuine*; combination form, *chalchiuh-*) and restricted its use to the emperor and the nobles.

NOMENCLATURE

The Friar Bernardino de Sahagun first referred to this stone as emerald in his monumental work on Aztec culture written in 1530, "*Historia general de las cosas de Nueva España*," and he was followed by later chroniclers, Peter Martyr (1530), Martinus de la Cruz (1552), Lopez de Gomara (1554), Molina (1571), Acosta (1590), Tezozomoc (1598), Herrera (1601-1615), Torquemada (1613), and finally Carochi (1645). That the so-called emerald was actually *chalchihuitl* is indicated by Tezozomoc, who refers to "emeralds and many other kinds of *chalchihuitl* stones," "Emeralds and other *chalchihuites*," etc. Herrera states that the Tlascalans called Cortes "*Calchihuitl*, which is as much to say Captain of Great Valor, because *chalchihuitl* is the color of emerald, and the emerald is highly prized among the natives." Molina in his early Mexican dictionary defines *chalchihuitl* as unpolished emerald, but "*esmeralda*" as "*quetzalitzli*."

Under the term *chalchihuitl*, the stone was also referred to by Cortes

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(1519a), Motilinia (1541), Molina (1571), Palacio (1576), Castañeda (1580), Herrera (1601-1615), Torquemada (1613), and Diaz del Castillo (1632).

Cortes (1519b), (except in his doubtful merced 1519a), and Duran (1585), refer to the material only as "greenstone." Those who define chalchihuitl simply as "precious stone" are Rincon (1595) and Vetancourt (1673).

There is no evidence that the indigenous population used this stone, except sparingly, for anything but ceremonial objects and ornaments. Compounded with various herbs, and with a green pearl added, the fine green chalchihuitl served in cures of a fracture of the head, for fever, gout, and it was even efficacious to revivify a dying person (Martinus de la Cruz, 1552). The Spanish conquerors enhanced its value further by imputing to it the virtue of alleviating pains of the side and the kidneys. A great many carved ornaments of chalchihuitl were brought to Europe from New Spain where they commanded fancy prices and brought high profits to the early freebooter. The physician Nicolas Monardes first mentioned them as *piedra de yjada*, or "stone of the loin" in his work on the medicines of the New World (1569). Others referring to this stone as *piedra de ijada* were Palacio (1576), Acosta (1590), Herrera (1601-1615), and Vazquez (1612). Translated into French this term became *Pierre de ejade* or, simply, *jade*. In the Latin translations of the Spanish works, the term became *lapis nephriticus*. The Latinized form gave rise to the mineralogical name *nephrite*, first used by Werner (1780).

Within fifty years after the Spanish conquest of Mexico, the supply of jade for amulet use became practically exhausted, because the stones in the possession of the nobles were by then already sold (Monardes), and the knowledge and appreciation of this gem in its original home was soon forgotten.

In the early 17th century a stone of somewhat similar qualities found its way into Europe from Persia, India and China, and, assuming the virtues of the American stone, became known also as jade. Damour (1846) investigated the Chinese material and recognized it as a form of tremolite, or "jade nephritique." Later (1863) he discovered a second mineralogical form of Chinese "jade," a sodium aluminum silicate, and a new species, which he named *jadeite*. Continuing his studies on jade, he found (1881) that jade objects from Mexico were also jadeite. By this time, however, the term jade had become so closely associated with the Asiatic stone that many authorities ignored the existence of the American mineral, or imputed to it an Asiatic origin. Dana did not recognize jadeite as a species until his 5th edition (1874), and then referred the mineral to the Chinese stone. Nephrite, he states, was brought from

Mexico or Peru, in the form of ornaments. It must now be recognized that in a historical and etymological sense jade, and jadeite, is an American stone.

CHEMICAL COMPOSITION OF CHALCHIHUITL

A recent study of Meso-American jade (Foshag 1954) demonstrates that the American stone includes a much wider range in physical aspect and mineralogical character than the Asiatic mineral. All Meso-American jade proves to be jadeite or its mineralogical congeners; no true nephrite has yet been found among the artifacts of that region. In previous investigations (Damour 1865), (Clarke and Merrill 1888), (Washington 1922), the samples analyzed contained varying proportions of albite (up to 90 per cent), and from such analyses attempts were made to calculate the composition of the jadeite portion. The new analyses, here given, were made upon carefully purified jadeite; the homogeneity of the samples was checked with the aid of the petrographic microscope.

Optical examination had shown that a considerable range of chemical variation was to be expected in the Meso-American jadeites. The analyses demonstrate that jadeite, diopside-jadeite, and chloromelanite are represented among the objects studied.

ANALYSES OF JADEITE

	1	2	3	4	5
SiO ₂	59.51	59.35	58.21	58.12	58.26
TiO ₂	0.01	0.18	0.04	0.31	0.04
Al ₂ O ₃	24.31	22.18	23.72	20.32	22.23
Cr ₂ O ₃	0.01		n.d.	0.01	none
Fe ₂ O ₃	0.35	1.15	0.91	2.49	0.71
FeO	0.03	0.32	0.24	0.77	0.21
MnO	0.01	0.01	0.04	0.07	0.03
MgO	0.58	1.77	1.20	2.16	2.18
CaO	0.77	2.57	1.79	3.13	3.72
Na ₂ O	14.37	12.20	13.07	12.43	11.91
K ₂ O	0.02	0.20	0.18	0.10	0.40
H ₂ O	0.06	0.20	0.46	0.16	0.44
	100.03	100.15	99.86	100.07	100.13

1. Jadeite, Burma. E. Zies, analyst, in Yoder (1950, p. 229).
2. "Blue jade," Mexico. Joseph Fahey, analyst.
3. Jadeite, rough, Manzanal, Guatemala. W. F. Foshag, analyst, in Foshag and Leslie (1955).
4. Jadeite, from pea green colored celt, Guatemala. Joseph Fahey, analyst.
5. Jadeite, from jade workers' tomb, Kaminaljuyu, Guatemala. Joseph Fahey, analyst.

ANALYSES OF DIOPSIDE-JADEITE

	1	2	3
SiO ₂	55.50	56.28	57.50
TiO ₂	none	0.03	
Al ₂ O ₃	12.33	12.18	12.10
Cr ₂ O ₃	none	none	
Fe ₂ O ₃	1.41	0.85	
FeO	1.33	1.28	
MnO	0.05	0.13	
MgO	8.72	9.02	9.60
CaO	12.76	12.60	13.40
Na ₂ O	6.94	6.94	7.40
K ₂ O	0.25	0.25	
H ₂ O	0.30	0.30	
	99.59	99.80	100.00

1. Diopside-jadeite (tuxtlite), Tuxtla Statuette. H. S. Washington (1922, p. 5).
2. Diopside-jadeite, rough fragment from tomb, Kaminaljuyu, Guatemala. Joseph Fahey, analyst.
3. Diopside-jadeite. Theoretical composition for Di₅₀Jd₅₀.

ANALYSES OF CHLOROMELANITE

	1	2
SiO ₂	57.39	56.45
TiO ₂	0.44	
Al ₂ O ₃	18.93	17.02
Cr ₂ O ₃	none	
Fe ₂ O ₃	4.45	7.62
FeO	0.81	
MnO	0.09	
MgO	1.92	2.32
CaO	2.74	4.76
Na ₂ O	12.46	11.46
K ₂ O	0.11	tr.
H ₂ O	0.54	
	99.88	99.63

1. Chloromelanite from grayish green celt, Guatemala. Joseph Fahey, analyst.
2. Chloromelanite pebble, Ouchy, Switzerland. Damour (1881).

VARIETIES OF CHALCHIHUITL

The finest and rarest quality of oriental jade is the so-called fei-t'sui, or king-fisher jade. Its color is emerald green, its diaphaniety is almost crystalline, and its luster on polished surface is pearly. A similar quality

of jade occurs among the Meso-American stone. Like the Chinese material, it is rare and occurs only in small pieces. It has been found in Olmecan pieces in the form of tubular beads and "jaguar claws."

Fine green jadeite, evenly colored or mottled with white, indistinguishable in many pieces from the fine Burma jadeite, is found in all cultures from the Pre-Classic (Archaic, Middle Cultures) to Aztec times. Some of the finest stone is found in Olmecan ear-plugs and figurines.

Celedon green jadeite, often coarse, distinctly grained, vitreous and uniformly colored, is a common form among the highland Mayan carvings. It shows little admixture of extraneous minerals. It resembles the pale forms of prehnite, which is also found among Meso-American artifacts.

A rather uniformly colored jadeite, without apparent grain, pale bluish-gray or greenish-gray, and varying in all nuances to dark ivy green to almost black, was much favored by the Olmecan artisans, and is almost the only jade known to the Nicoyans of Costa Rica. A common feature is the presence of white ghost-like spots within the body of the translucent stone.

Another distinct form of jadeite is uniformly pale gray in color, opaque with a texture of stubby reticulated prisms. It was widely used for celts among the highland Maya, and occasionally fine carved masks in the Olmecan culture.

A pea-green vitreous jadeite, evenly colored and textured, is abundant in the form of celts among the highland Mayan cultures.

A bright to dark green jade (diopside-jadite) widespread among the Mayan cultures, is often indistinguishable from the green forms of jadeite, except by careful examination.

A very dark green to black stone is the ferrian form of jadeite, chloromelanite, not unlike the European chloromelanite in composition. It is common in Guatemala in the form of celts and other utilitarian tools, and occasionally in objects of artistic merit. It has been found in all highland cultures from the Archaic to the Colonial, and ancient celts recovered at archeological sites are still used by Guatemalan potters.

Among the Aztecs, chalchihuitl was the most precious of substances. As an indication of its value, one may quote Moctezuma's words, as recorded by Bernal Diaz del Castillo (1632), upon an occasion of paying tribute to Cortes: "I will also give you some very valuable stones, which you will send to him in my name; they are chalchihuites and are not to be given to anyone else but only to him, your great Prince. Each is worth two loads of gold." The greatest virtues were comparable to this stone. A father, addressing his daughter upon reaching the age of discretion, tells her "Although you are but a little damsel, you are as precious as a chalchihuite" (Sahagun 1530).

The Aztecs had their nomenclature to distinguish the various grades or categories of this stone. The generic term was *chalchihuitl*. Mena (1927) derives this term from *xalli*—sand, *xihuitl*—herb, that is, a granular herb-colored stone. Objection can be made to Mena's derivation of *xihuitl* as "herb" or "herb-colored," since this root appears in the names of other gem stones that are not green; e.g., *teoxihuitl* (turquoise), *tlapalteoxihuitl* (amethyst). Another, and perhaps more logical derivation is from *xalli*—sand or sandstone, *xuihtic*—green or blue, *iuitl*—plumage of birds; that is, a granular stone the color of a bird's green plumage.¹ Since the plumage of certain tropical birds were used extensively in adornment, and were considered of great value, the comparison of a precious stone with precious plumage is logical in the poetic speech of the Aztecs.

Sahagun describes *chalchihuite* as "green and not transparent mixed with white." This is the common variety of jade often seen in Meso-American objects, and is similar in appearance to the modern Burmese jadeite.

Quetzalchalchihuitl: *Quetzalli*—feathers of the *quetzallototl* (the quetzal), *chalchihuitl*—jade; that is, jade the color of the plumage of the quetzal. Sahagun states "it is very green and has no spots, and is transparent and very green; those that are not have spots and streaks." Molina defines it as "precious stone of a blue or green color." This is the high quality jade as one sees it in fine Olmecan pieces, and is comparable in appearance to rich, evenly colored Burmese jade.

Iztacchalchihuitl: *Iztac*—white, *chalchihuitl*—jade. Sahagun describes this stone as "white with veins of green or clear blue, also they have other colors mixed with the white."

The etymology of the word and Sahagun's description suggest that this stone is the white variety of jadeite, or jadeite mixed with albite. Both forms are not uncommon among Mexican and Guatemalan objects.

Quetzalitzli: Of this stone Sahagun remarks, "The emeralds that are called *quetzalitzli*, of which there are very good ones in this land, of great value, are so-called because *quetzalli* means very green feather, and *itzli* obsidian, and which is highly polished and without spot or flaw, which are characters of good emerald."

Sahagun was the first to refer to "esmeralda" in Mexico, but no occurrence of emerald is known in Meso-America, and no emeralds have been found in archeological sites north of Panama. It is suggested, here, that this stone is the finest quality of jade, similar to the Chinese *fei-t'sui* jade, emerald green in color, flawless, and almost transparent. This opinion is supported by Monardes, who states that the finer qualities of

¹ Nahuatl is a highly agglutinative language, in which many roots may be combined into a single formidable word.

"piedra de ijada," that is, chalchihuitl, resemble emerald. Both Molina and Carochi define quetzalitztl as "emerald."

Tlilayotic: *Tillic*—black, *ayotic*—adjectival form of *ayotl*, gourd, that is dark gourd colored. According to Sahagun, it "is a form of chalchihuitl, a mixture of green and black."

Leon (1938) renders this term malachite. Sahagun classes it among the jaspers. The word does not appear in Molina. The mineral referred to probably represents chloromelanite.

Xiuhtomolli, *xiuhtomoletl*: *xiuhclic*—green or blue; *tomo*—bone; *tell*—stone; a green or blue bone-like stone. Sahagun describes it "is like chalchihuitl, green and white mixed, it is beautiful." "They bring it from Guatemala and Soconochó." The green and white color suggests amazonstone. Some of the amazonstone from this region may be said to have a bone-like aspect. Both Molina and Carochi render the word as turquoise. It was used in mosaics in the same manner as turquoise. Good examples of amazonstone are found among the artifacts of Guatemala. It is probably not chalchihuitl as Sahagun suggests.

Sahagun also mentions "chalchihuites fingidos," false chalchihuitl, used by the common people to whom the use of chalchihuitl was denied. This may have been any one of the lesser stones found in archeological deposits, probably the mottled green metadiorite.

OCCURRENCE

The widespread use of jadeite in hard-stone carvings in Meso-America, and the lack of an evidence of a local provenience have led some students of early American cultures to postulate an extraneous source of this material, possibly the Orient. This postulate ignores the fact that many varieties of Meso-American jade have not been found anywhere else in the world. Since the oriental jadeite was unknown until its discovery in Burma in the 18th century, A.D., the use of jadeite in America antedated its use in the Orient by more than 2,000 years.

All known occurrences of jadeite *in situ* are associated with serpentine (Burma, Chibber 1934; California, Yoder and Chesterman 1951; Japan, Iwao 1953; Celebes, de Roever 1955). In all cases albite is an important and intimate associated mineral. Minerals occurring as minor accessories are quartz, analcime, nepheline, pectolite, actinolite or tremolite, garnet, lawsonite, mica, chlorite, natrolite, zoisite and sphene.

The Meso-American jadeite frequently contains abundant low-temperature albite ($\alpha = 1.526 - 1.528 \pm .001$, $\gamma = 1.537 - 1.539 \pm .001$), much of the stone varying from albitic jadeite to jadeitic albite. Other accessory minerals in this jadeite are muscovite, common but not abundant; sphene, hornblende, actinolite, zoisite, and chromite, all rare. In the chloromelanite, albite is rare; garnet, sometimes common; sphene, anal-

cime, epidote, hornblende and glaucophane, rare.

The character of the Meso-American jadeite, and its mineral associates suggest that, like jadeite in other occurrences, it will be found in close association with serpentine.

Recently an occurrence of jadeite has been discovered near the village of Manzanal in the Motagua valley of Guatemala, in close proximity to the serpentine area of the Sierra de las Minas (Foshag, W. F., and Leslie, Robert 1955). The nature of the find and the character of the stone suggest that it was a source of material for some of the ancient indigenous cultures, particularly of the highland Mayan cultures of the Quiché region of Guatemala. Archeological finds in and about the Motagua valley further suggest that this region was a center of jade-working and dispersal (Foshag 1954).

Other areas of serpentine that may contain jadeite deposits are the Sierra de Chuacas, along the north slope of the Motagua valley; an area south of the Rio Negro, extending from Zacapulus to Santa Rosa; and an area along the western shore of Lake Yzabel; all in Guatemala; and a small area near Chimalapa, Chiapas, Mexico (Sapper 1937). A small area near Tehuitzingo, Puebla, was examined for jadeite by the writer, without success. Another small area in Mexico near Victoria, San Luis Potosi, presumably is beyond the limits of the cultures that appreciated jade.

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WATER AND OTHER VOLATILES IN VOLCANIC GLASSES*

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ABSTRACT

The two phases of volcanic glass, represented by obsidian enclosed in perlite, provide a key to origin and relations not available where either one occurs alone. The perlite has formed through the hydration of obsidian after emplacement. The H_2O content of obsidian is commonly a few tenths of one per cent, and that of perlite 2 to 5 per cent. The H_2O in these two types of glass is in such a different state of combination that the proportional effect in increasing the index of refraction is several times as great in obsidian as in perlite. This provides a method for determining the different modes of origin of volcanic glasses. The index of refraction before and after dehydration is determined and the difference divided by the water content. The resulting ratio provides definite criteria.

The studies of Shepherd indicate that the hydration resulting in the development of perlite at the expense of obsidian has tended to flush magmatic types of volatiles out of the system. These relationships indicate that the water and other volatiles in obsidian are pristine, being derived from the parent magma, whereas the water of perlite is the result of a later episode.

INTRODUCTION

Volcanic glasses have long interested geologists, as they represent a chilled phase of original magma and commonly contain volatile constituents that are believed to represent, at least in part, pristine magmatic materials. The water content of glasses and the wide variation in its proportion have been a subject of much study, and some work has been done on the relation of water to physical properties. However, the full significance of the relationship between physical properties and variations in the volatile content of volcanic glasses presents a fruitful field of research.

Volcanic glasses occur abundantly in the Valles Mountain region of northern New Mexico, and an investigation of some of these was begun as a part of the study of that volcanic region by Ross and Smith. Early in the study it became evident that volcanic glasses presented relationships, some of which had not previously been recognized. This encouraged extending the study to include selected samples from other regions in the belief that this would provide pertinent information about some of the problems of volcanology.

Also it was evident that the mass spectrograph offered a new approach to the study of volatiles in glasses and could aid the general study of glassy rocks. Irving Friedman of the Geological Survey had become interested in the deuterium content of such glasses, and it seemed that

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both these modes of approach would be benefited by an integrated study. Thus, there has been a close coordination of the two methods of investigating volcanic glasses. However, it has seemed advisable to present the results of the index of refraction-water relationships in this paper, and those of the deuterium-hydrogen relationships in a second paper, which will appear in a later issue of this journal.

As commonly happens, new problems have arisen along with new information, and the present paper cannot attempt to follow through all of the avenues suggested. Nor is this the place to discuss possible geologic applications. However, a stage has been reached which seems to justify a presentation of the results that have been attained.

The present study applies only to rhyolitic, dacitic, and related glasses and the conclusions reached apply only to them. Basaltic and andesitic glasses seem to constitute a distinct and somewhat different problem, but data on a few such glasses are included for purposes of comparison.

ACKNOWLEDGMENTS

The study of volcanic glasses has been aided by the hearty cooperation of others interested in the problems presented. A number of the samples were received from the U. S. National Museum. Mr. Charles W. Chesterman of the California Division of Mines is engaged in a detailed study of the perlite and obsidian deposits of California and has been very helpful in contributing several sets of specimens of perlite-obsidian from that state. Dr. Tómas Tryggvason of the University Research Institute, Reykjavik, Iceland, sent us several specimens of perlite and one of perlite-obsidian. Professor Tom F. W. Barth has provided obsidian from Hekla, Iceland, and Robert G. Schmidt has provided perlite from Mojave, California, and "vitrophyre" from Saipan, western Pacific. Mr. J. J. Reed, New Zealand Geological Survey, kindly sent us a very useful set of specimens from that country. Joseph J. Fahey of the Geological Survey has been of great assistance in making dehydration tests of glasses and determining specific gravities.

PERLITE-OBSIDIAN PAIRS

General description

In many occurrences of glassy rhyolitic rocks, two types of glass have developed. One is typical obsidian and the other typical perlite, the perlite normally being the dominant material. The obsidian commonly occurs as small pellets enclosed in perlite as illustrated in Plate 1, Fig. *a*. In thin section the obsidian pellets occur as cores surrounded by the concentrically cracked perlite as illustrated in Plate 1, Fig. *b*. These ob-

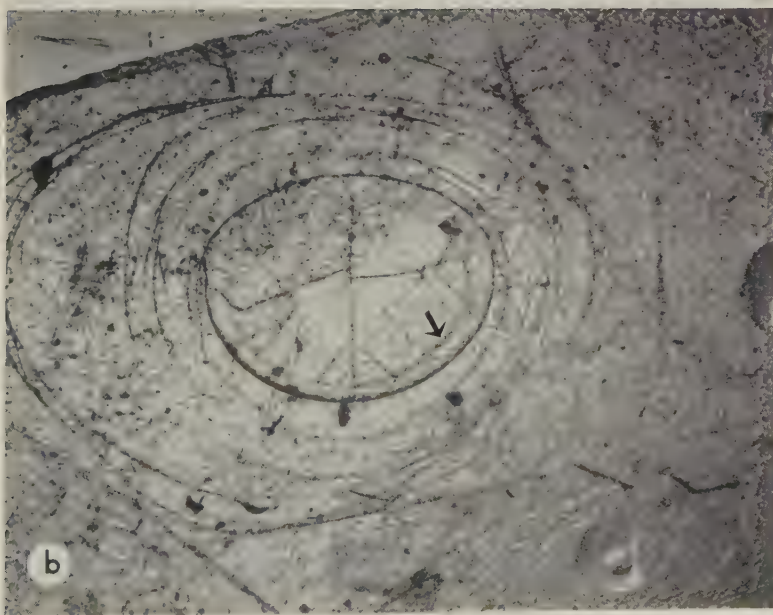
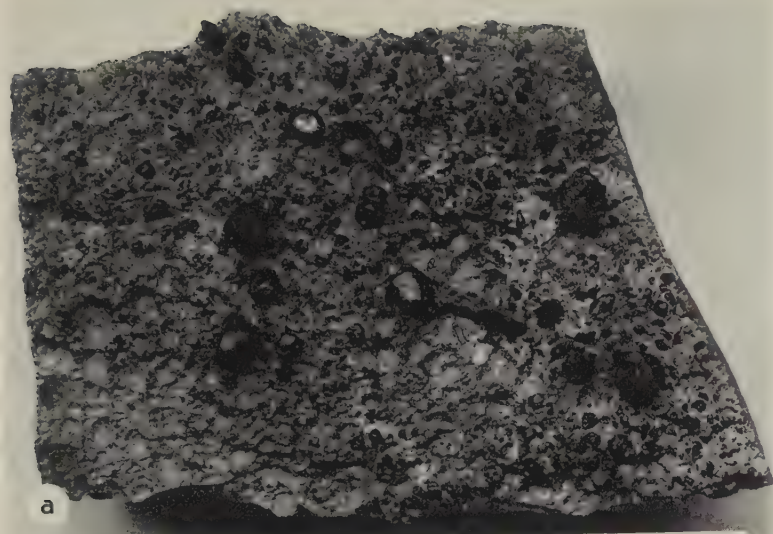


PLATE 1

FIG. *a*. Hand specimen from 1½ miles west of Polvadera Peak, Valles Mountains region, New Mexico. Collected by Smith. Illustrates obsidian cores (dark) enclosed in perlite (gray). Numerous pits represent places where cores have broken out. ½ natural size.

FIG. *b*. Thin section showing perlite with perlitic cracks, enclosing non-hydrated core. The arrow marks the boundary between the core with a much lower index of refraction than the enclosing perlite. The fractures within this core formed on the release of strain during grinding. From Arroyo Hondo, Valles Mountains region, New Mexico. Magnification $\times 30$.

sidian cores have been called *marekañite* (Judd, 1886, p. 241-248), and their origin has long been a subject of speculation.

The occurrence of two types of glass occurring in pairs presents evidence about their genetic history that is lacking when either obsidian or perlite is considered alone. In these occurrences there is a sharp boundary between perlite and obsidian, giving direct evidence of a sequence in their formation. The only interpretation that seems possible is that the entire mass was originally obsidian and the perlite was formed as a result of some secondary process. Thus the pairs provide a key which permits the development of criteria for the differentiation of these distinct phases and brings into contrast the differences in their physical and chemical properties.

In hand specimens obsidian is usually black, but much of that from the Valles Mountains region of New Mexico is perfectly transparent in plates up to 3 millimeters thick and with only a slight smoky color. Where trichites are unusually abundant the obsidian may be gray. In general the obsidian contrasts strongly with the light-colored perlite. However, the obsidian also occurs as very small cores in perlite as illustrated in Plate 2, Fig. *a* and these tend to merge in color with the perlite.

The writers have examined perlite-obsidian pairs from 8 different occurrences; four from the Valles Mountains region, New Mexico, one from Cerro No Agua, New Mexico, one each near Olancho and Clear Lake, California, and one from Iceland, and one pumice from Mono craters, California.

A hand specimen from about $1\frac{1}{2}$ miles west of Polvadera Peak, Valles Mountains region, New Mexico, shows the relation between perlite and obsidian cores. In the Arroyo Hondo locality of the same region, the cores range up to 8 cm. in diameter, those about 15 mm. in diameter being most abundant. The material from this locality is unusually low in the minute trichites which characterize most volcanic glass, the obsidian is remarkably transparent, and the relationships are representative of perlite and obsidian in general. For this reason many of our more detailed experiments have been based on this material.

The other occurrences of volcanic glass need no detailed description. All the obsidians studied are similar to those discussed in connection with the obsidian-perlite pairs. So-called pitchstones seem to include several types of glass. Some are a dull gray due to the development of an unusually large proportion of trichites, and do not differ essentially from other obsidians, which also commonly contain trichites. Some, especially those with a greenish color, have undergone alteration and do not form a part of this study. The larger cores are also characterized by a hydrated film, although this is not as obvious as in those that can be

examined under the microscope. However, this hydrated film is shown by the development of a vesiculated film on heating the cores.

In Table 3 a group of hydrated glasses is listed. This includes typical perlites, pumices, and rocks which would commonly be described as flow rocks, but which are also characterized by perlitic structures. Many of these contain varying proportions of phenocrysts, and in a few the phenocrysts were removed by heavy solutions before study.

Microscopic relations

In addition to the cores that are so conspicuous in the hand specimen, the perlite from several localities contains smaller but similar cores which are observable only under the microscope. Selected grains of such material from Arroyo Hondo, New Mexico, are illustrated in Plate 2, Fig. *a*. These vary in size to as little as about 0.04 mm. in diameter, those about 0.15 mm. being most characteristic. In this material the outer zone has a water content of about 3.5 per cent and the cores about 0.3 per cent. The index of refraction of the cores is about 1.486 and that of the enclosing perlite about 1.497. This large difference results in the strong contrast illustrated in Plate 2, Fig. *a*. The perlites from Prestahnukur, and Cerro No Agua, contain cores similar to those from Arroyo Hondo.

This sharp boundary is of especial interest, as it might be expected that diffusion of H_2O into the glass would result in a transitional boundary between the two phases. However no such transitional boundary is observable in any of the specimens studied, even with very high magnifications.

Plate 2, Fig. *b* illustrates the same cores as Plate 2, Fig. *a* under crossed nicols, and shows the strain birefringence which is observable in almost all such cores. This strain birefringence has been described by Judd (1886, p. 241–248) as a part of his study of the “marekanites” from near Okhotsk, Siberia.

There appear to be two types of strain represented in the cores in Plate 2, Fig. *b*. The conspicuous outer zone, which is white in the photomicrograph, is probably related to the hydration of the outer rims. The inner part shows a fainter, more shadowy birefringence that seems to be independent of the narrow outer zone. This is especially conspicuous in grains up to 10–15 mm. in diameter, although it seems to be absent in very large ones. It is questionable whether the formation of a hydrated film 0.03 to 0.05 mm. in thickness would develop strain throughout the core and for a distance several hundred times as great as the thickness of the hydrated border. The outer birefringence disappears on heating, while the inner one persists.

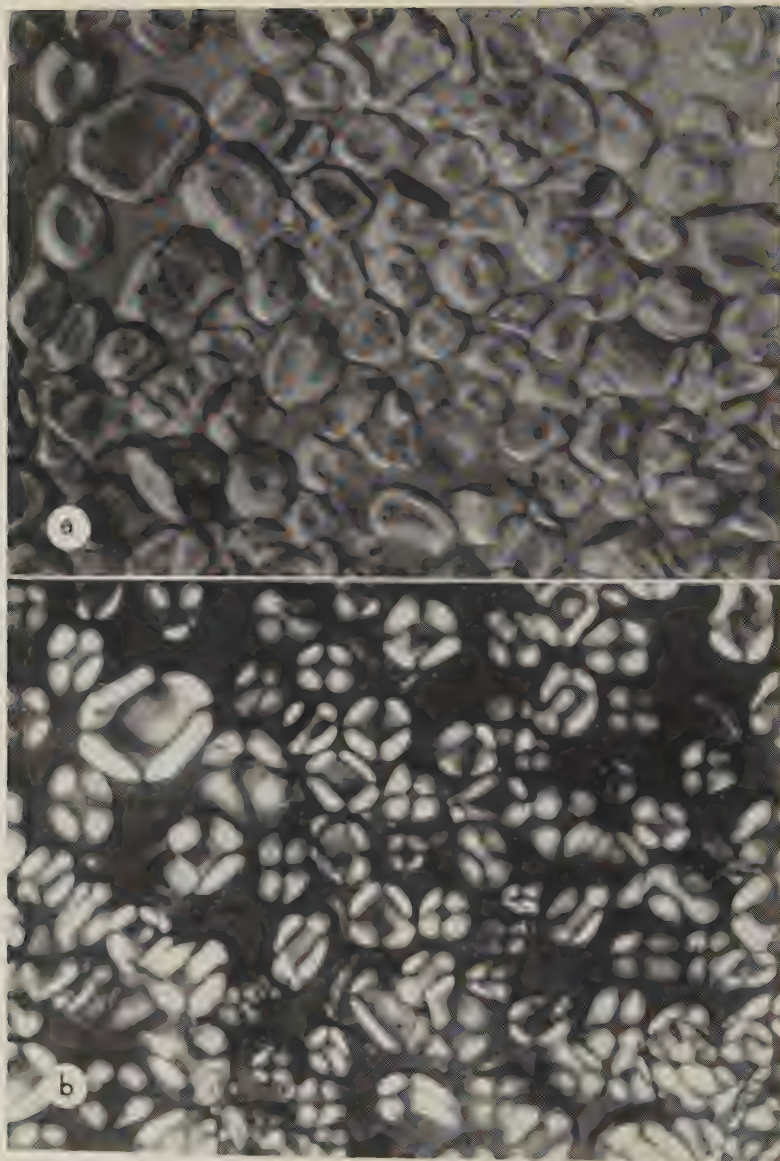


PLATE 2

FIG. *a*. Glassy beads from Arroyo Hondo. Two phases of glass composed of inner cores of low-water glass (0.3% H₂O) enclosed by hydrated glass (1.5% H₂O). The contrast between the two is due to the difference in the indices of refraction. Cores $n=1.486$, rims (perlite) $n=1.496$. Magnification $\times 27$.

FIG. *b*. The same glass grains under crossed nicols, showing strain birefringence. The strongest birefringence on the border, coincides with the hydrated outer rim. The inner part shows a weaker birefringence.

The glass surrounding the obsidian cores shows the characteristic perlite structure, but there are great differences in the perfection of its development. An unusually good example of an area of perlite with onion-like structure surrounding a nonhydrated core, is illustrated in Plate 1, Fig. *b*.

Chemical composition

All the glasses considered in this paper are rhyolitic in character. Most of those for which chemical analyses are available have a silica content from 75 to nearly 78 per cent (water free). One of the least silicic glasses included in this study is that from Little Glass Mountain, California (Shepherd 1938, p. 328), with $\text{SiO}_2 = 73.59$ per cent.

The H_2O content of the obsidian ranges from about 0.1 to 0.9 per cent in 19 specimens available for study. Most commonly the H_2O content is of the order of a few tenths of a per cent. The hydrated glasses, of which 23 were studied, range from around 2 to about 5 per cent H_2O . A very large proportion have between 3 and 4 per cent H_2O . A further discussion of volatiles is included below.

Methods of study

The study of volcanic glasses has involved two distinct methods of approach. One of these has been a determination of the differences in amount of the H_2O and a correlation of this with the physical properties of the glass and in particular with the indices of refraction. The other approach has been the determination of the deuterium-hydrogen ratio of the water in solution in the glass.

Index of refraction determinations

The problems involved seemed to demand very exact determinations of the indices of refraction, especially for the low-water obsidians with their small differences in these indices. For most of the obsidians it was possible to grind and polish surfaces and measure indices of refraction on a refractometer using sodium light. Some glasses gave an optically perfect line of total reflection. In others the line was somewhat hazy and the mean of several readings was used.

The indices of refraction of perlite, pumice, and dehydrated glasses were determined in index oils. The accurate results desired made advisable the use of the double inclined illumination method developed by Saylor (1953). This accentuates contrasts until differences of index of refraction in the 4th decimal place are observable. For this study a special set of index oils with very small intermediate steps was prepared and checked at frequent intervals. Further refinement was obtained by

mixing these oils, drop by drop, and by repeated checks. Temperatures were kept within close limits. Close checks between refractometer and index oil determinations were obtained. It is believed that these methods and the checks gave results significant in the 4th decimal place for much of the glass. Some of the glasses were slightly variable and results significant only in the 3rd decimal place were obtained.

Determinations of volatiles

Two methods have been used in the determination of the volatiles in glasses. One involves weighing, heating to thorough fusion (about 1050° C. in most glasses), and reweighing. The other involves the direct weighing of the H₂O as a part of the deuterium-hydrogen determinations. The first method gives the total volatiles, whereas the second gives the H₂O content directly. Only small differences in the results of the two methods were observable in the study of rhyolitic glasses.

Most of the rhyolitic glasses are so low in ferrous iron that the oxidation of any part of this would have no material effect on the loss of weight on heating. This was confirmed by the method of direct weighing.

Preliminary experiments indicated that most of the H₂O in glass, and in particular that above a few tenths of a per cent, seems not to be held under equilibrium conditions. However, loss of H₂O at successive temperatures between 200° and 1050° C. and for uniform periods of heating was determined on representative samples. These experiments showed that loss of H₂O was far more dependent on length of heating at successive steps than upon actual temperatures. The dehydration curves based on these data seemed to provide no essential information and therefore have not been reproduced. However, it is significant that in our experiments all but about 0.3 per cent of the H₂O of perlite can be driven off by continued heating at temperatures below 600° C., whereas that above that figure is held with much greater tenacity. The tenacity with which water in perlite is held at different temperatures has been studied by King, Todd, and Kelley (1948).

More significant data on the relation of H₂O content to indices of refraction were obtained by determining the water loss on representative samples (those from Arroyo Hondo), at closely spaced intervals of water loss. At each successive stage in H₂O loss, material was removed for index of refraction determinations. The results are presented in Table 4, and the relation indicated by the curves in Fig. 1.

The studies of the escape of volatiles from glasses and the vesiculation at fusion temperatures have presented some interesting relationships which probably have bearings on some aspects of volcanism. However, these need not be considered here.

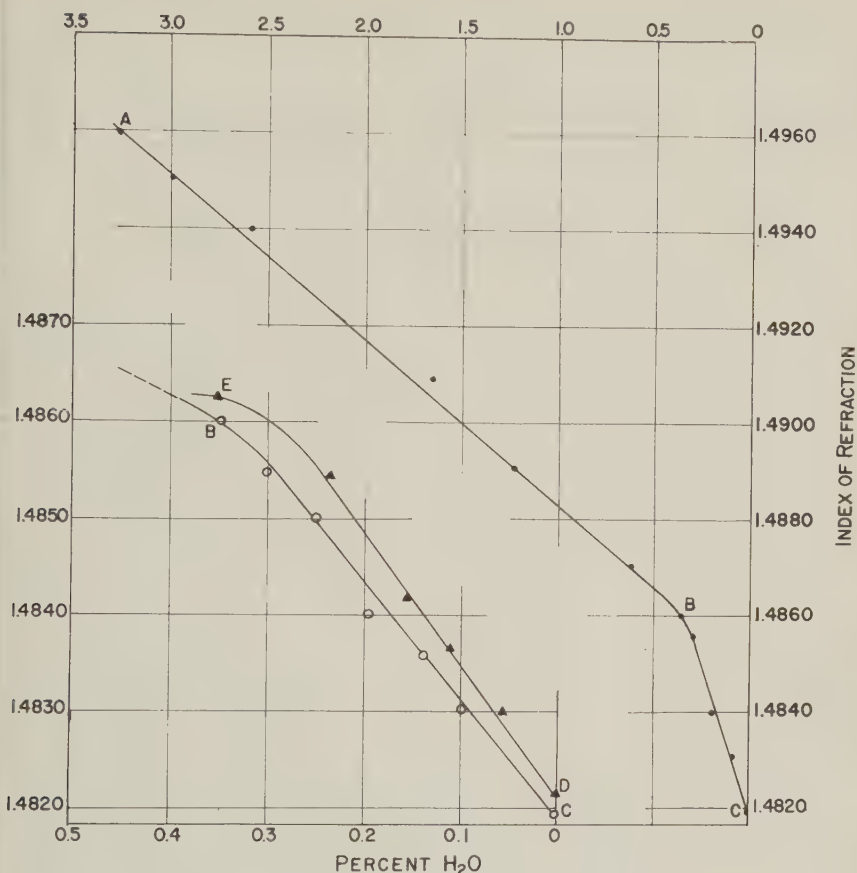


FIG. 1. Relationships between water content and indices of refraction for Arroyo Hondo glasses. The upper curve represents the relationship for perlite. The lowest of the three curves represents that part of the curve for perlite lying between the points *B* and *C* plotted on the larger scale. The third curve *E-D* presents the same relationships for the obsidian plotted on the same scale.

Tilley (1922) points out that the indices of refraction of rhyolitic glasses rise with increasing water content.

Specific gravity

The specific gravity of the obsidian from Arroyo Hondo is 2.34. On dehydration the weight loss equaled the water loss. Most of the perlite and all of the pumice contain vesicular cavities which prevent meaningful specific gravity determinations. However, the specific gravity of the perlite from Arroyo Hondo is 2.37 as against 2.34 for the obsidian from

which it was derived. About 3.5 per cent of H_2O has been added without a corresponding change in specific gravity—that is, with only a small change in volume. The marked birefringence illustrated in Plate 2, Fig. *b*, which has developed as a result of hydration, is no doubt related to this addition of water without a corresponding change in volume. The rise in the index of refraction with the addition of water of hydration is no doubt a part of the same relationship.

Discussion of observations

The large obsidian inclusions (marekanites) in perlite have long been recognized, but the small ones (Plate 2, Fig. *a*) recognizable only under the microscope are more informative. In these the sharpness of the contact between the two glass phases is shown. It is evident that the high-water rims immediately around the cores have been formed at their expense. Successive outer shells all have similar relations, and it seems evident that all the perlite (i.e., all the high-water glass) has formed from obsidian. This addition of water (hydration) evidently occurred after emplacement of the original glass.

Relation of indices of refraction to water content

Eight occurrences with two phases of glass present as obsidian and perlite and one of pumice and obsidian have been available for study. The relation between H_2O content and indices of refraction are presented in Table 1. The indices of refraction before and after dehydration (n_b and n_c) are given; the difference between these is listed and also (w) the H_2O loss in per cent. The difference in the numerical value of the two indices of refraction was divided by water content of the glass. This gives a ratio, shown in the last column of the table, which represents the relative effect of water on the index of refraction of the glass. The same relationship is presented for a group of obsidians in Table 2 and for a group of hydrated glasses in Table 3.

In the perlite of the perlite-obsidian pairs represented in Table 1 the H_2O content ranges from about 3 to 3.5 per cent, or about 10 times that in the obsidian cores. In some of the hydrated glasses of Table 3, H_2O content is as much as 5 per cent, and some of the obsidians of Table 2 contain 0.1 per cent H_2O or less.

These tables show that the relationship of water to index of refraction is surprisingly consistent. Of course, it is best for the high-water glasses where plus or minus errors in determinations of H_2O content or of indices of refraction have a minor effect on the resulting ratio. In the group represented in Table 1, only in *7b* (representing a pumice from Mono Craters) is the ratio materially out of line. This is probably due to the fact that

TABLE 1. RELATIONS BETWEEN WATER CONTENT AND INDICES OF REFRACTION OF PERLITE-OBSIDIAN GLASSES

No.	Character	Indices of Refraction			Water loss in per cent w	$\frac{n_h - n_e}{w}$
		n_h	n_e	$n_h - n_e$		
1a	Obsidian*	1.4860*	1.4820*	0.0040	0.32	0.0125
1b	Perlite	1.4957	1.4818	0.0139	3.21	.0043
2a	Obsidian	1.4860*	1.4817	0.0043	0.33	.0130
2b	Perlite	1.4962	1.4821	0.0141	3.22	.0044
3a	Obsidian	1.4862*	1.4817	0.0045	0.35	.0128
3b	Perlite	1.4976	1.4818	0.0158	3.20	.0049
4a	Obsidian	1.4865*	1.4825	0.0040	0.35	.0114
4b	Perlite	1.4985	1.4824	0.0161	3.45	.0047
5a	Obsidian	1.4854*	1.4820	0.0034	0.30	.0113
5b	Perlite	1.4963	1.4821	0.0142	3.45	.0041
6a	Obsidian	1.4860*	1.4821	0.0039	0.33	.0118
6b	Perlite	1.4980	1.4821	0.0159	3.40	.0047
7a	Obsidian	1.4863	1.4818	0.0045	0.35	.0129
7b	Pumice	1.494	1.482	0.012	1.9	.0063
8a	Obsidian	1.4885	1.4858	0.0027	0.22	.0123
8b	Perlite	1.498	1.485	0.013	3.5	.0038
9a	Obsidian	1.488	1.477	0.011	0.9	.0122
9b	Perlite	1.495	1.479	0.016	3.5	.0045

* Measured on refractometer.

LOCALITIES OF PERLITE-OBSIDIAN GLASSES

1a, 1b—Arroyo Hondo, Valles Mountains region, New Mexico, upper glass horizon.

2a, 2b—Arroyo Hondo, Valles Mountains region, New Mexico, lower glass horizon.

3a, 3b—Obsidian Ridge, Valles Mountains region, New Mexico.

4a, 4b—1 mile SW of Bear Springs, Valles Mountains region, New Mexico.

5a, 5b—Cerro No Agua, near Tres Piedras, New Mexico.

Nos. 1a, 1b to 5a, 5b, collected by Ross and Smith.

6a, 6b—Prestahnukur, Iceland. Received from Dr. Tómas Tryggvason, Reykjavik, Iceland.

7a, 7b—Mono Craters, Calif. Collected by Irving Friedman.

8a, 8b—Near Lower Lake, California }
9a, 9b—Near Olancho, California. } Contributed by Charles W. Chesterman.

Mono Craters are very young and the pumice is only partly hydrated.

In Table 2, No. 7, the obsidian from Mayor Island, New Zealand, gives a ratio that is low compared with the other members of the group. However, the numerical figures are so small that an error of 0.01 per cent in determination of the H_2O , or of 0.0002 in the indices of refraction would explain the discrepancy. The value 0.0075 is still such as to align the Mayor Island glass with other obsidians. Other members of the

TABLE 2. INDEX OF REFRACTION-WATER RELATIONS OF OBSIDIANS

No.	Indices of Refraction			Water loss in per cent w	$\frac{n_h - n_e}{w}$
	n_h	n_e	$n_h - n_e$		
1	1.4843*	1.4827	0.0016	0.11	0.0145
2	1.4832*	1.4815	0.0017	0.11	.0155
3	1.4842*	1.4820	0.0022	0.20	.0110
4	1.4850*	1.4805	0.0045	0.32	.0141
5	1.4883*	1.4867	0.0021	0.19	.0110
6	1.4946*	1.4934	0.0012	0.10	.0120
7	1.4878*	1.4872	0.0006	0.08	.0075
8	1.4905*	1.4893	0.0012	0.10	.0120
9	1.4910*	1.4898	0.0012	0.10	.0120
10	1.4834*	1.4820	0.0014	0.12	.0117

* Measured on refractometer.

OBSIDIAN LOCALITIES

- 1 mile NW of the Puerto de Abrigo, Valle Toledo quad., Valles Mountains region, New Mexico.
- Obsidian Knob, $1\frac{1}{2}$ mi. S.W. of Polvadera Peak, Valles Mountains region, New Mexico. Nos. 1 and 2 collected by Ross and Smith.
- Ascension Island, South Atlantic. Received from U. S. National Museum, Museum No. 36281.
- Norwikakat River, Alaska. Received from U. S. National Museum, Museum No. 6384.
- Mt. Hekla, Iceland. Received from Prof. Tom F. W. Barth.
- Harfntinnuhyggur, Iceland. Received from U. S. National Museum, Museum No. 88428.
- Mayor Island, New Zealand. Received from U. S. National Museum, Museum No. 70345.
- Little Glass Mountain, Calif. Received from Donald E. White.
- Big Glass Mountain, Calif. Received from Donald E. White.
- Osidian Cliff, Yellowstone National Park. Collected by Irving Friedman.

group with about 0.10 per cent H_2O fall into line with those with 0.30 per cent H_2O .

The outstanding relationship shown in Tables 1, 2 and 3, is the very large difference in the effect of water, in its several forms, upon the indices of refraction of the two types of glass. The ratio $(n_h - n_e)/w$ for 9 obsidians of Table 1 ranges from 0.0113 to 0.0130, with a mean of 0.0122. For 8 perlites (omitting the partly hydrated pumice), this ranges from 0.0038 to 0.0049, with a mean of 0.0044. The effect of H_2O in raising the index of refraction is over $2\frac{1}{2}$ times as great in obsidian as in perlite. This large difference must be due to the way in which H_2O is held in the two glasses. The obsidians of Table 2, and perlites and pumices of Table 3

TABLE 3. INDEX OF REFRACTION-WATER RELATIONS OF HYDRATED GLASSES

No.	Character	n_h	n_e	$n_h - n_e$	Water loss in per cent w	$\frac{n_h - n_e}{w}$
1	Perlite	1.4957	1.4789	0.0168	4.33	0.0039
2	Pitchstone	1.4950	1.4805	0.0145	3.22	.0045
3	Pitchstone	1.4966	1.4810	0.0156	3.86	.0040
4	Perlite	1.4982	1.4811	0.0171	4.20	.0041
5	Perlite	1.4950	1.4802	0.0148	4.00	.0037
6	Pumice	1.503	1.485	0.018	3.80	.0047
7	Welded tuff	1.500	1.487	0.013	2.85	.0045
8	Pumice	1.520	1.496	0.024	5.3	.0045
9	Pumice	1.520	1.505	0.015	4.0	.0037
10	Perlite	1.498	1.483	0.015	3.7	.0040
11	Pitchstone	1.499	1.483	0.016	4.5	.0035
12	Perlite	1.496	1.482	0.014	4.45	.0032
13	Perlite	1.495	1.420	0.013	2.96	.0044
14	Perlite	1.500	1.485	0.015	3.85	.0039

LOCALITIES OF HYDRATED GLASSES

1. Perlite, Bear Jump, Peralta Canyon, Valles Mountains region, New Mexico.
2. Perlite $1\frac{1}{2}$ mi. NW of Bland, Valles Mountains region, New Mexico.
3. Brown glass, Bears Head, Valles Mountains region, New Mexico.
4. Perlite, $1\frac{1}{4}$ mi. SSE of Bears Head, Valles Mountains region, New Mexico.
5. Perlite, mouth of Colle Canyon, Valles Mountains region, New Mexico.
6. Pumice, El Cajete, Valles Mountains region, New Mexico.
7. Obsidian-like welded tuff, Ammon Quad., southeastern Idaho. Specimens 1 to 7 collected by Ross and Smith.
8. Pumice, from 2 kilometers west of Mexico-Michoacan boundary, on Mexico-Guadalajara Highway, collected by Carl Fries.
9. Pumice, from 3 kilometers west of Tenango Highway, State of Mexico, Mexico. Collected by Carl Fries.
10. Perlite, Black Canyon, NW $1/4$ Opal Mt. Quadrangle, Calif. Collected by Robert G. Schmidt.
11. Pitchstone, Saipan, Pacific Ocean. Collected by Robert G. Schmidt.
12. Perlite from Sarashene-gou, of Shinano, Japan. Received from U. S. National Museum, Museum No. 11857.
13. Perlite from Nagngiho, $3\frac{1}{2}$ mi. NNW of Wairakei on Waihruru stream, New Zealand.
14. Perlite, Earthquake Flat, 12 mi. south of Rotorua, New Zealand. Nos. 13 and 14 were received from Dr. J. J. Reed, New Zealand Geological Survey.

vary a little more from the mean, but present the same relationships.

We have observed only one glass with the character of an obsidian in which there may be a question about its origin. A glass from Xalapazguillo, Puebla, Mexico, submitted by Carl Fries of the Geological Survey,

had an H_2O content of 0.89 and an index of refraction of 1.4864 before, and 1.4825 after dehydration, giving a ratio of 0.0044. By the criteria outlined, therefore, it should be a hydrated glass notwithstanding its obsidian character. Its most conspicuous difference is strongly contrasting bands of dark- and light-gray glass. The relations lead to a tentative suggestion that this obsidian represents a magma which was erupted into a moist environment where it became hydrated at a temperature, possibly of 600°C . or less, that is below a temperature at which the water assumes combinations giving the higher effect on the index of refraction.

Additional information about H_2O -index of refraction relationships is presented by the curves shown in Fig. 1. Here indices of refraction have

TABLE 4. OBSIDIAN AND PERLITE FROM ARROYO HONDO, WATER-INDEX OF REFRACTION RELATIONS

Perlite		Obsidian	
H_2O (Per cent)	Index of refraction	H_2O (Per cent)	Index of refraction
3.35	1.4960	0.345	1.4862
3.00	1.4950	0.245	1.4855
2.60	1.4940	0.155	1.4842
1.71	1.4910	0.110	1.4836
1.25	1.4890	0.049	1.4830
0.64	1.4870	0	1.4822
0.30	1.4855		
0.19	1.4840		
0.10	1.4830		
0	1.4819		

been plotted against the amount of H_2O held in the obsidian and perlite from Arroyo Hondo. On the smaller scale the curve shows two parts (*A* to *B* and *B* to *C*) with a very distinct change in the inclination at the point ($n=1.4857$, $\text{H}_2\text{O}=0.3$). The curves plotted on the larger scale show that the curve for obsidian (*E* to *D*) corresponds with that part of the curve (*B* to *C*) for perlite lying between 0 and 0.3 per cent H_2O . That is, the curves show that the water of hydration in perlite has been added to the original glass represented by obsidian without affecting the original H_2O .

The foregoing relations mean that the true effect of the water of hydration is exemplified by that portion of the curve lying between points *A* to *B*, where $n=1.496$ and 1.486. The difference between the two is about 0.010 and the H_2O loss about 3 per cent. Therefore the figure for

the corrected ratio becomes $0.6101/3=0.0034$ as compared with 0.0127 for obsidian. If the calculation is based on the relations between the points between *A* and *C* we have $1.496-1.4819=0.0141$ and $w=3.35$, giving $0.0141/3.55=0.0039$. In other words, the effect of H_2O on the index of refraction as corrected is in fact nearly $3\frac{1}{2}$ times as great for obsidian as for perlite. Thus the ratios expressing the relation between H_2O and indices of refraction for hydrated glasses in Tables 1 and 3 are in fact the mean effect of two states of water. For purposes of determination, however, the figures given in these tables are adequate, and there should be no doubt as to which group the specimen belonged.

THE STATE OF WATER IN GLASS

The cause of the large difference in the effect of water on the indices of refraction of the two types of glass—that in obsidian and that with

TABLE 5. GASES FROM ROCKS IN VACUO (SHEPHERD, 1938, p. 326)

(Volume percentages)

No.	CO ₂	CO	H ₂	N ₂	A	Σ ₂	Cl ₂	F ₂	H ₂ O
Obsidians (Rhyolitic)									
1	1.402	0.705	0.101	2.897	0.000	0.367	2.965	3.163	88.386
2	1.595	0.035	0.174	1.420	0.000	0.014	0.499	0.516	96.299
3	0.179	0.073	0.501	3.897	0.002	0.000	1.820	7.795	89.246
4	0.075	0.008	2.253	1.153	0.000	0.039	1.498	2.205	94.434
5	0.672	0.007	0.377	0.138	tr.	0.000	1.713	4.329	92.761
6	0.077	0.032	0.080	0.053	udt.	0.000	0.069	1.136	98.551

water of hydration—is not clear. We are only sure that there must be some marked difference in the way water is combined. It is commonly believed that in a solution, such as glass, the different ions are present in essentially all possible combinations. The determination of the character of these combinations presents a difficult problem in physical chemistry, and an evaluation of those combinations as they affect indices of refraction poses an even more difficult one.

In studies of gases in artificial glass Harrison (1947, p. 362–366) and also Florence and associates (1950, p. 121–128) report the presence of OH among the volatiles present in glass at fusion temperatures. Keller and Pickett (1954, p. 87–98) also have reported OH among the forms of water present in perlite, especially that proportion (about 1.12 per cent) retained at higher temperatures. Water is evidently present in glass in several forms, but the way these combine with silica and other constituents to control indices of refraction is problematical.

CHEMICAL COMPOSITION OF VOLATILES

By remarkably good fortune a pair of glasses, which are a part of this study, were investigated by Shepherd (1938) in his classical study of water in glasses. The following Table 5 from that paper (p. 326) gives the volatile content of 3 pairs of glasses, nos. 5 and 6 being those of the Cerro No Agua glasses. Our data on the relation between H_2O and the indices of refraction of these glasses are given in Table 1, nos. 5a and 5b.

No. 5 of the foregoing Table 5, called black obsidian by Shepherd, represents the low-water glass, and material called "pitchstone" by Shepherd, is the same glass after hydration. The significant changes here shown are the large losses, particularly of CO_2 , Cl_2 , and F_2 , and the gain in H_2O on the change of obsidian into "pitchstone." That is, hydration has had the effect of flushing these volatiles from the system and replacing them by H_2O in the hydrated glasses.

Our studies of the Cerro No Agua glasses have shown that the perlite (pitchstone of Shepherd) has about 3.35 per cent of H_2O which agrees closely with Shepherd's determination of 3.10 per cent (Shepherd, 1938, p. 329). On the other hand we have found only about 0.3 per cent of H_2O in the obsidian as a result of numerous tests. We now know, as Shepherd could not have known, that the obsidian cores have an outer hydrated film. Thus there is a strong probability that the H_2O determined for the "pitchstone" by Shepherd was in part water of hydration. This in no way detracts from the definite evidence of change in the composition of the water. It merely suggests that the difference in the composition of the two states of water may have been even greater than indicated.

Shepherd made similar determinations on "dense black obsidian" and "pumiceous phase of the same block" from Big Glass Mountain, California (nos. 1 and 2), and on "dense black obsidian" and a "coarsely vesiculated portion of same block" from Coso Mountains (nos. 3 and 4). These tests show the same trend in the removal of CO_2 , Cl_2 , and F_2 with an increase in H_2O as in the Cerro No Agua materials.

SOURCE OF WATER IN GLASS

The probable explanations of water in normal obsidian is that it was inherited directly from the magma, that is, it represents pristine H_2O . The very large difference in the effect on the indices of refraction shows that the water in perlite and obsidian was fixed under very different conditions. The fact that the H_2O of obsidian is held tenaciously and released almost explosively at temperatures of 800° to 1000° C. indicates fixation at temperatures characteristic of magmas. The data presented by Shepherd (1938, p. 326) show that obsidian is characterized by im-

portant proportions of CO_2 , CO , Cl_2 , S_2 , and F_2 —volatiles probably derived directly from a magma.

The water of hydration may have been derived from volatiles escaping at depths from the cooling magma. However, the water of hydration was deficient in other volatiles and so water derived from a magma seems to present a doubtful source. A distinctly post-magmatic episode, probably the result of rain, snow, or ground water seems more probable. This reaction could occur during a late cooling stage or at a still later time.

BASALTIC AND ANDESITIC GLASSES

As previously stated, basaltic and andesitic glasses seem to present a somewhat different problem from that of the rhyolitic ones. For this

TABLE 6. INDICES OF REFRACTION OF BASALT-ANDESITE GLASSES

No.	Character	Indices of Refraction			Water loss (w)
		n_h	n_e	$n_h - n_e$	
1	Basalt (pumice)	1.597	1.600	+0.003	0
2	Basalt	1.598	1.598	0	1.2
3	Basalt (Pele's hair)	1.603	crystallized on cooling		1.2
4	Basalt (thread pumice)	1.600		0	3.35
5	Andesite (pumice)	1.536	1.536	-0.006	4.75

LOCALITIES OF BASALT AND ANDESITIC GLASSES

1. Pumice formed at the surface of the 1948 summit flow, Mauna Loa.
2. Beach pellets formed where the 1950 flow from Mauna Loa entered the ocean near Hoopuloa. Collected by Jewell J. Glass.
3. Pele's hair from Mauna Loa.
4. Thread pumice or "reticulite" from near Volcanic Observatory, Kilauea, collected by Chester K. Wentworth.
5. Andesitic pumice from Paso de Cortes between Ixtaccihuatl and Popocatepetl volcanoes.

reason such glasses have not been included in this study. Also the small tendency for basaltic magmas to form glasses and the very ready alteration of such glasses are handicaps to such a study. However, the reader will be interested in data on a few basaltic glasses for purposes of comparison, and the data for 4 such glasses, all from Hawaii, are given in Table 6. The basaltic glasses have indices of refraction not far from 1.600, and the andesitic glass from the pass between Popocatepetl and Ixtaccihuatl, Mexico, has an index of refraction around 1.530. The notable thing about the basaltic glasses is that their indices of refraction show

little response to water content. With actual alteration of basaltic glasses the effect on physical properties, of course, becomes important. The indices of refraction of a group of basaltic glasses are listed by Tilley (1922, p. 279).

The basaltic glasses are so high in ferrous iron that the relations between water content and oxidation of ferrous iron would all be inter-related. A detailed study of all these would be necessary for any definitive study of basaltic glasses.

SUMMARY

Three independent methods of study have shown that volcanic glasses are of two types, each with distinctive properties. The relation between water content and indices of refraction indicates that there must be a marked difference in the physical state of the two types of water. An earlier study by Shepherd shows distinct different proportions of certain volatiles (CO_2 , CO , F_2 , S_2 , and Cl_2) in the two types of glass. When interpreted in the light of later geologic studies there is a new significance added to the classic study of Shepherd. We believe that this will lead others, as it has us, to an increased appreciation of his work.

One type of glass (obsidian) is believed to be characterized by pristine water derived from the magma, and the other (hydrated) to be the result of a later episode probably unrelated to magmatic processes. The relations present a seemingly clear-cut method for distinguishing between glasses with pristine water and those which have undergone later hydration. The glasses characterized by pristine water contain under 1 per cent of H_2O in those available for study. The hydrated glasses have an H_2O content ranging most commonly from 3 to 5 per cent. If, as seems evident, the H_2O in the high-water glasses is the result of post magmatic processes, these glasses high in water present no evidence about the amount of H_2O in the magma from which they are derived. On the other hand the glasses with pristine water do not set a limit on the amount of water in the magma from which they were derived. This is because we have no way of determining the amount of water lost by diffusion during the eruption and emplacement of the magma, or during the vesiculation of a pumice.

The very small amount of water necessary for the vesiculation of a glass and the development of a very large proportion of voids, has interesting geologic implications which can not be developed here.

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TWO CHLORITES: GONYERITE AND MELANOLITE*

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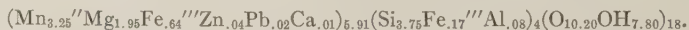
ABSTRACT

Gonyerite is a new manganese member of the chlorite group. Analysis gave: MgO 11.55, CaO 0.07, MnO 33.83, PbO 0.56, ZnO 0.42, Fe₂O₃ 9.42, Al₂O₃ 0.58, SiO₂ 33.06, Ti and As nil, H₂O+ 10.31, H₂O- 0.02; total 99.82. Apparently orthorhombic, pseudohexagonal, with $a_0=5.47$, $b_0=9.46$, $c_0=28.8$ Å. Color deep brown; gravity= $3.01 \pm .04$ meas., 3.03 calc. Optically negative, with $n_X=1.646$ (dark brown), $n_Z=1.664$ (light olive brown); $2V=0^\circ$. Found as radial aggregates of laths with barite and bementite in hydrothermal veinlets at Långban, Sweden.

The ill-defined mineral melanolite described by Wurtz in 1850 from Somerville, Massachusetts, is shown to be a (lepto-) chlorite identical with delessite. Analysis: Na₂O 0.17, K₂O 0.07, CaO 1.10, MgO 10.71, FeO 20.96, MnO 0.18, Fe₂O₃ 10.46, Al₂O₃ 13.77, TiO₂ 0.16, SiO₂ 29.94, H₂O+ 10.00, H₂O- 2.48; total 100.00 after deducting CaCO₃. Optically negative, with $n_X < 1.63$ (light olive green), $n_Z=1.650$ (dark olive green); $2V$ small to 0° . Gravity=2.73; spacing d_{001} 14.4 Å. Data are given for both gonyerite and melanolite on the change in x-ray pattern and optics on heating to 500° .

GONYERITE

The unusual new manganese member of the chlorite group here noted virtually lacks aluminum. The chemical analysis (Table 1), calculated on the basis of 18(O, OH) with Al and enough Fe''' assigned to fill the tetrahedral positions, yields the following formula:



The significant excess of divalent cations appearing when the Fe is calculated as divalent and either (Si, Al) is taken as 4 or (O, OH) as 18, suggests that the ferric iron in large part at least is primary. Pennantite, the only other known high-manganese chlorite (1), is rich in Al (18.60 per cent Al₂O₃) and relatively low in Mg and Fe'''.

The x-ray powder pattern closely resembles those of the chlorites in the position and relative intensity of the (00*l*) reflections, and includes the diagnostic 14 Å line, but many of the fainter lines differ. (The pattern of pennantite is identical with that of thuringite from Schmiedefeld.) There also is definite evidence that the *c*-axis identity period is 28 Å and not 14 Å. Weissenberg photographs from minute cleavage flakes were marred by disorientation effects, and although no reliable information as to symmetry could be obtained they indicated an orthorhombic cell with $a_0=5.47$, $b_0=9.46$, $c_0=28.8$ Å. The mineral is dimensionally pseudohexagonal since $b_0=\sqrt{3}a_0$. A fairly satisfactory indexing of the

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TABLE 1. CHEMICAL ANALYSIS OF GONYERITE

	1	Iron as Fe'''	Iron as Fe''
MgO	11.55	Mg = 1.954	2.000
CaO	0.07	Ca = .008	.008
MnO	33.83	Mn = 3.252	3.327
PbO	0.56	Pb = .017	.017
ZnO	0.42	Zn = .035	.036
Fe ₂ O ₃	9.42	Fe''' = {	Fe'' = .823
Al ₂ O ₃	0.58		
SiO ₂	33.06	Al = .078	.079
H ₂ O+	10.31	Si = 3.754	3.840
H ₂ O-	0.02	O = 10.197	10.018
		OH = 7.803	7.982
	99.82		

1. Gonyerite. Långban, Sweden. Analysis by F. A. Gonyer, 1952. Ti and As absent.

powder photograph is afforded by this cell (Table 2). The spacings are the largest yet reported for a chlorite, due to the high content of Si and of the relatively large Mn'' ion.

The mineral occurs at Långban, Sweden, associated with barite, berzeliite, bementite and garnet in small hydrothermal veinlets cutting skarn. It forms rounded radial aggregates of laths and plates up to several millimeters in length. A few tiny aggregates of apparently hex-

TABLE 2. X-RAY POWDER DATA FOR GONYERITE

Iron radiation, manganese filter, in Ångströms. Indexing for orthorhombic cell with $a_0=5.47$ Å, $b_0=9.46$, $c_0=28.8$

<i>I</i>	<i>d</i>	<i>hkl</i>	<i>d</i> _{calc.}	<i>I</i>	<i>d</i>	<i>hkl</i>	<i>d</i> _{calc.}
3	14.6	002	14.4	2	2.888	00.10	2.88
$\frac{1}{2}\dagger$	8.0	012	7.90	2	2.801		
10	7.23	004	7.20	3	2.697	202	2.69
$\frac{1}{2}^*$	5.79	005	5.76	1	2.610	00.11	2.61
						211	2.61
1*	5.33	101	5.37	$\frac{1}{2}$	2.550	204	2.55
5	4.79	006	4.80	1	2.441		
8	3.61	008	3.60	$\frac{1}{2}$	2.056	00.14	2.05
						231	2.05
1	3.33	123	3.35	$\frac{1}{2}^*$	1.696	00.17	1.69
$\frac{1}{2}$	3.22	009	3.20	3	1.634		
$\frac{1}{2}$	3.13	030	3.15	5	1.574		
$\frac{1}{2}$	3.03	033	3.00	1*	1.437	00.20	1.44

* broad line.

† = very broad line.

agonal plates intergrown in the manner of "iron-roses" were observed. The bementite forms buff-colored aggregates of small lamellar-fibrous grains. A manganoan variety of penninite has been described by von Eckermann (2) from Långban, but this mineral is normal in composition, with MnO 1.06, Al₂O₃ 16.17, Fe₂O₃ 0.56, and is distinct from the present species.

Color is deep brown with reddish internal reflections; powder milk-chocolate brown. Cleavage (001) perfect; foliae are flexible but inelastic. Hardness 2½. Gravity 3.01 ± .04. The gravity calculated from the cell and the formula first given is 3.03. Optically negative with 2V = 0°; *n*X or *n*E = 1.646 (dark brown), *n*Z or *n*O = 1.664 (light brown) in white light. Rapidly decomposed by cold concentrated HCl and slowly by cold 3N HCl with the separation of flaky-gelatinous silica; insoluble in cold concentrated H₂SO₄. After heating at 500° for 30 minutes the mineral becomes brownish black in color. There is no change in the powder pattern, other than an increased diffuseness, eliminating some of the fainter lines, and a very marked increase in the intensity of the 14.4 Å line over the 7.2 Å line. There is an accompanying small decrease in the spacings of (00*l*). Optically the heated material shows high birefringence and much decreased absorption in brown. The indices are greatly increased, with *n*Z, somewhat variable, ranging up to 1.84. The differential analysis curve places the breakdown of the brucite-type layer at about 600°.

The presence of the 14 Å line in unheated material and the behavior on heating indicate that this mineral structurally is of the chlorite type. The increase in intensity of the 14 Å line and the decrease in (00*l*) spacing on heating is typical of high-iron chlorites. The name gonyerite is proposed for this mineral after Forest A. Gonyer, analytical chemist, associated for many years with this Department and now retired.

Gonyerite differs from the problematic manganese silicates bementite (with which gonyerite is associated), ectropite and caryopilite both chemically, in its large content of ferric iron and magnesium, and structurally. Since bementite appears to be related in structure to antigorite and gonyerite to the chlorites there are certain analogies between them, both in the formula ratios and the diffraction patterns. Thus the 7 Å and 3.5 Å powder lines are common to both, but bementite lacks the 14 Å line and differs otherwise. Larsen (7) and Pardee, Larsen and Steiger (8) have held on optical and chemical grounds that caryopilite, ectropite and bementite are identical, and Larsen suggests that bementite is a manganese member of the serpentine group. Caryopilite and ectropite were here found to give identical powder patterns, and this pattern is very close to that of bementite; both patterns are similar to, but not quite identical with, that of antigorite. Gonyerite differs com-

pletely in properties and powder pattern from the following manganese and iron silicates: gageite, leucophoenicite, alleghanyite, parsettensite, manganpyrosmalite, friedelite, schallerite, ganophyllite, macgovernite and cronstedtite. Among Långban minerals, gonyerite closely resembles in outward appearance the manganese arsenite-silicate dixenite.

Melanolite (= Delessite)

This chlorite was described in 1850 by H. Wurtz (3) from the long-abandoned Milk Row diabase quarry on Granite Street, Somerville, Massachusetts. The petrography of the diabase has been described by

TABLE 3. CHEMICAL ANALYSES OF MELANOLITE

	1	2	Iron as given	Iron as Fe''
Na ₂ O	1.85	0.17	Na = .04	.04
K ₂ O		0.07	K = .01	.01
CaO		1.10	Ca = .13	.13
MgO		10.71	Mg = 1.74	1.79
FeO	25.09	20.96	Fe'' = 1.92	2.84
MnO		0.18	Fe''' = .86	6.01
Fe ₂ O ₃	23.13	10.46	Mn = .02	.02
Al ₂ O ₃	4.48	13.77	Ti = .01	.01
TiO ₂		0.16	Al { 1.04	{ 1.17
SiO ₂	35.24	29.94	.73	.65
H ₂ O+}	10.21	10.00	Si = 3.27	3.35
H ₂ O-}		2.48	O = 10.71	10.53
			OH = 7.29	7.47
	100.00	100.00		

1. Melanolite. Somerville, Massachusetts. Analysis of Wurtz (1850) given as recalculated to 100 by Wurtz after deducting 12.77 per cent CaCO₃.

2. Melanolite. Somerville, Massachusetts. Analysis by E. H. Oslund, University of Minnesota, 1954. Recalculated to 100 from original sum of 99.55 after deducting CO₂ 1.81 as CaCO₃.

Jaggar (4). The original analysis of Wurtz (Table 3) was made on very impure material and is faulty in other regards. Dana (5) classed melanolite as an ill-defined chloritic material, and the mineral has not been noticed in modern reviews of the chlorites. X-ray and thermal study of specimens from the collections of Harvard University and Wellesley College indicate that melanolite is a chlorite, and a new chemical analysis is cited in Table 3. The high content of ferric iron and the deficit of six-coordinated ions place the mineral as a leptochlorite. The analysis corresponds exactly to an orthochlorite, however, when the iron is all calculated as Fe'' (Table 3). The content of Fe''' is regarded as secondary and due to oxidation, in contrast to gonyerite.

Melanolite falls in the composition field of delessite in the classification of Hey (6). The name melanolite apparently has priority over delessite, but in any case it should be abandoned in favor of the widely used name delessite. Melanolite appeared in the July issue of the 1850 volume of the *American Journal of Science* (the paper itself is dated April 1, 1850), while delessite appeared in the 1850 edition of Naumann's *Mineralogie* (foreword dated July 6, 1850).

Melanolite occurs as dense, slickensided lamellar coatings along joint planes and fissures in the diabase. Thin films of a slightly ferroan calcite ($n_O \sim 1.661$) penetrate between the foliae. Color black with a greenish tinge. Streak and powder olive green to greenish gray. Gravity = 2.73 (2.69, Wurtz). Easily soluble in cold concentrated HCl and slowly in cold 3N HCl with separation of flaky to granular semigelatinous silica; insoluble in cold concentrated H_2SO_4 . Optically biaxial negative with $2V$ small to 0° ; $n_X < 1.63$ (light olive green), $n_Z = 1.650$ (dark olive green) in white light. The x-ray powder pattern is very similar to that of thuringite, but with the unusual feature that the 14 \AA line is darker than the 7 \AA line, opposite to the rule in the chlorites. The spacing d_{001} is 14.4 \AA . On heating to 500° for 30 minutes the 14 \AA line is preserved in position and relative intensity. The heated material, brown in color, has high birefringence and diminished absorption in brown. The indices are greatly increased, with n_Z variable and ranging up to 1.86.

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NOTE ADDED IN PRESS

Recent correspondence with Dr. Frans E. Wickman of the Royal Museum, Stockholm, has shown that the mineral here described as gonyerite had been recognized as a new species many years ago by G. Aminoff, although a description never had been published. The following analysis, an average of two, was made in 1937 by R. Blix.

(Na, K) ₂ O	MgO	MnO	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	SiO ₂	H ₂ O—	H ₂ O+	Total
0.31	12.22	32.89	0.50	9.90	nil	32.84	1.01	9.96	99.63

X-RAY INVESTIGATION OF FERRIERITE, A ZEOLITE

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ABSTRACT

Ferrierite was named and described in 1918 by R. P. D. Graham. The Kamloops Lake locality is its only reported occurrence. An x -ray study of the mineral indicates cell dimensions: $a_0 = 19.12 \pm 0.06$ Å, $b_0 = 14.14 \pm 0.03$ Å, $c_0 = 7.48 \pm 0.02$ Å and an orthorhombic body centered lattice. The choice of axes is Graham's and departs from the conventional orthorhombic orientation in which $c < a < b$. The following space groups are compatible with the x -ray observations: *Immm*, *I222*, *Imm2*, *I2₁I2₁I2₁*. Tests for piezoelectricity in liquid nitrogen were negative or inconclusive. From the cell content calculation a general formula of $(\text{Na}, \text{K})_4\text{Mg}_2(\text{Si}_{30}\text{Al}_6)\text{O}_{72}(\text{OH})_{218}\text{H}_2\text{O}$ is indicated. Although ferrierite, because of its high magnesium content, is unusual among zeolites, rehydration and other tests point to a tectosilicate framework structure rather than a sheet structure, and consequently it is considered to be a true zeolite.

INTRODUCTION

Ferrierite was described by R. P. D. Graham in 1918 and named in honor of the late W. F. Ferrier of the Canadian Geological Survey. To date, the only locality from which ferrierite has been reported is the north shore of Kamloops Lake in British Columbia where it occurs as spherical aggregates of radiating blades enclosed in chalcedony. This chalcedony fills seams in basalt flows of the Kamloops Volcanic Group of lower Miocene age, according to Graham (1918). A complete description of the petrology of the area and the occurrence of ferrierite is given in Graham's paper.

The presence of almost 3% magnesia in ferrierite makes it unusual among zeolites. Likewise of interest is the high silica content which is over 69%. Silica-rich heulandite (clinoptilolite) and mordenite approach ferrierite in silica content, but most zeolites only contain silica in the range between 40% and 60%. The high content of magnesia, together with the platy structure of ferrierite, raises some doubt as to whether or not the mineral is a zeolite. This problem was considered in the present investigation.

ACKNOWLEDGMENTS

The first material used for x -ray and optical study was obtained from the Geological Museum of Harvard University through the kindness of C. Frondel. Later, additional material was given by R. P. D. Graham. The x -ray work was carried on in the Mineralogical Laboratory of the University of California, Berkeley. Professor A. Pabst contributed a great deal to the study, not only in making valuable suggestions but in actually assisting in much of the x -ray work.

PHYSICAL PROPERTIES

In the present study, in addition to a re-examination of the recorded data on ferrierite, additional information was obtained using x -ray methods. Graham's earlier work, without benefit of x -rays, proved to be accurate and very satisfactory.

Graham measured two of the indices of refraction by total reflection, and also the size of the obtuse optic axial angle. From these he calculated the size of the acute optic axial angle and the third index of refraction. The indices determined in immersion liquids during the present investigation were within 0.002 of Graham's, which is within the usual limit of error.

Graham oriented the crystals with a -axis $= \alpha$, b -axis $= \beta$, c -axis $= \gamma$. He notes, "in each case compensation takes place when the quartz wedge is inserted normal to the length." For this to be true his quartz wedge must have been cut from the less usual position with its length parallel to the c -axis of the quartz crystal. Graham states that crystals are tabular parallel to (100) and elongated parallel to the c -axis. This orientation is most common, but it is also true that some crystals are tabular parallel to (100) but elongated parallel to the b -axis. This difference in elongation aided in the x -ray work.

In regard to the orientation of the crystals, Graham's orientation has been followed. This leads to $c < b < a$ rather than the conventional $c < a < b$ for the orthorhombic system.

Graham determined the specific gravity to be 2.150, but he did not state the method used in making the determination. A precise determination is difficult; air spaces between the tabular crystals tend to give values too low, and included chalcedony raises the values. Occasionally opal is present along with the chalcedony. Westphal balance determinations made on small grains carefully selected under the microscope gave the best results and indicates the specific gravity of 2.15, suggested by Graham as acceptable.

Correlation with morphology. Graham reported the angle $100 \wedge 101 = 67^\circ 47'$, obtained by measuring 2 or 3 crystals with minute (101) faces yielding only faint images. This corresponds to $c:a = 0.4084$. X -ray measurements lead to a ratio of $c_0:a_0 = 0.3922$, which would require that the angle $100 \wedge 101$ be $68^\circ 35'$.

X-RAY DATA

Powder photographs taken with copper radiation and a nickel filter gave sharp lines and led to the data in Table 1. Lines with d_{hkl} less than 2.5 \AA were not indexed. Seven Weissenberg and precession patterns were fully indexed over this range to aid in obtaining the powder pattern indexing.

TABLE 1. INDEXED PORTION OF POWDER PATTERN OF FERRIERITE

<i>hkl</i>	<i>d</i> _{calc.}	<i>d</i> _{meas.}	<i>I</i> _{obs.}	<i>hkl</i>	<i>d</i> _{calc.}	<i>d</i> _{meas.}	<i>I</i> _{obs.}
110	11.38	11.33	2	501	3.41	3.42	2
200	9.56	9.61	10	240	3.32	3.31	2
020	7.07	7.00	3	600	3.19	3.20	1
101	6.97			141	3.15	3.15	3
011	6.61	6.61	2	312	3.14		
310	5.81	5.84	5	222	3.12	3.07	3
220	5.68	4.96	1—	521	3.07		
211	5.44			431	3.06		
121	4.96			530	2.97	2.97	3
301	4.85	4.80	1—	402	2.95	2.90	2
400	4.78			620	2.905		
130	4.57	4.58	1—	132	2.896		
321	4.00	3.99	9	611	2.871	2.72	2
031	3.99			341	2.857		
420	3.96	3.88	1	440	2.842		
411	3.87			150	2.798	2.64	2
330	3.79			422	2.719		
002	3.74	3.79	2	710	2.682		
510	3.69	3.69	5	332	2.662	2.58	3
231	3.68	3.54	8	051	2.645		
112	3.55			512	2.627		
040	3.53			350	2.585	2.566	3
202	3.48	3.49	8	042	2.569		
				701	2.566		
				251	2.549		

Additional lines, not indexed:

2	2.49	2	2.11	4	1.78	1—	1.55	2	1.37
2	2.43	2	2.04	1—	1.72	2	1.50	1	1.34
4	2.37	3	2.00	2	1.65	2	1.47	1	1.27
1—	2.32	B3	1.94	B2	1.63	3	1.43	2	1.25
1—	2.26	3	1.87	2	1.60	1—	1.41		

Lines marked B are broad.

CELL DIMENSIONS AND SPACE GROUPS

From Weissenberg and precession patterns, using copper and molybdenum radiation and correcting for shrinkage, the cell dimensions obtained were:

$$a_0 = 19.12 \text{ \AA} \pm 0.06 \text{ \AA}$$

$$b_0 = 14.14 \text{ \AA} \pm 0.03 \text{ \AA}$$

$$c_0 = 7.48 \text{ \AA} \pm 0.02 \text{ \AA}$$

A study of the Weissenberg and precession patterns leads to the conclusion that the only systematic extinction occurs for *hkl* when *h*+*k*+*l*

is even. This is also evident from indexing of powder patterns and fulfills the requirements for a body-centered lattice. No additional extinctions indicating glide planes could be established and consequently the following space groups are consistent with the x-ray data: *Immm*; *I222*; *I2₁2₁2₁*, *Imm2*.

Robert M. Douglass and Edward Clark, then graduate students at the University of California, kindly assisted in carrying out tests for piezoelectricity in liquid nitrogen on five selected crystals. Results of repeated trials on all five crystals were negative or inconclusive. A positive result would have been an indication for the group *Imm2*, but lacking evidence of this it is not possible to select any one uniquely.

CELL CONTENT OF FERRIERITE

Because of the lack of sufficient pure material, no new chemical analyses have been made, and the cell content determined here is based on Graham's analysis.

Cell volume: $19.12 \text{ \AA} \times 14.14 \text{ \AA} \times 7.48 \text{ \AA} = 2022.26 \text{ \AA}^3$

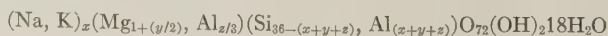
Density: 2.15

Cell weight: 4347.86×10^{-24} grs.

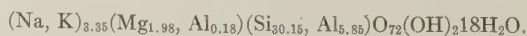
Graham's Analysis		Number of Atoms in Cell	
SiO ₂	69.13 wt. %	Si	30.15
Al ₂ O ₃	11.44	Al	5.88
CaO	none	Mg	1.895
MgO	2.92	Na	3.35
Na ₂ O	3.97	K	0.20
K ₂ O	0.36	H	37.94
H ₂ O	13.05	O	91.76
	100.87		

The number of atoms in the cell was determined using a weight for the unit of atomic weight of 1.6602×10^{-24} grs.

As will be noted, the sum of Si + Al is near 36 and the number O - H/2 is near 72, so O/(Si + Al) is close to 2/1, a ratio characteristic of the zeolites. Based on a general formula



a possible formula close to the actual one would be



The actual formula based on Graham's analysis is



which is close to the theoretical formula. Rounded off with simple subscripts, this would suggest the formula for ferrierite:



In the generalized formula suggested first above there is no guide as to the range of values for x , y , z , as no comparison with other members of a series can be made, and there is no definite knowledge of the structure. Consequently, no limits of variation for x , y , z , are given, although they undoubtedly exist.

STRUCTURE

The formula suggested requires a framework structure of linked (Si, Al) O_4 tetrahedra sharing all corners with 2 additional negative ions (OH) for every 36 linked tetrahedra. An example of this type of structure in which anions are added to the framework is shown by scapolite and cancrinite, although a specific example of added (OH) ions is not known.

The single eminent cleavage of ferrierite $a(100)$ and the long spacing normal to this cleavage ($a_0 = 19.12 \text{ \AA}$) might be considered to indicate a sheet structure. However, rehydration experiments indicate most of the water is not firmly bound and hence probably not involved in the sheet structure. Ferrierite heated at 125° for 30 minutes lost 2.73% H_2O and on standing 2 days regained almost all (98.8%) of the lost water. Heating at 250° for 30 minutes caused a loss of 6.21% of which almost all (97.7%) was regained in 24 hours. This high degree of rehydration indicates that a tectosilicate structure is most probable and that the mineral is a true zeolite.

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ALLUAUDITE

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ABSTRACT

Alluaudite is described from a Black Hills pegmatite. Alluaudite is monoclinic, probably $C2/c$ (possibly Cc), with $a:b:c=12.004:12.533:6.404\text{\AA}$, $\beta=114^{\circ}22'$. The six stronger lines in a powder photo (Fig. 1) are: 2.73/10, 6.27/8⁻, 3.07/7, 2.51/7⁻, 5.47/6⁻, and 3.49/6⁻. Powder data appear in detail in Table 1. The optical orientation is $[b]\sim\gamma$, and $\beta\wedge[c]=+18.5^{\circ}$. The dispersion of the birefringence is given in Table 2. The chemical analysis of the Black Hills alluaudite appears in Table 3.

INTRODUCTION

Alluaudite from a pegmatite near Chanteloube in west-central France was described by Damour in 1848. While it is discussed in Dana's System (1892) as an alteration product of Fe-Mn phosphates, it later was neglected and so was not mentioned in Ford-Dana's Text or the Larsen-Berman tables. It was resurrected in 1937 by Quensel for the Varuträsk (Sweden) paragenesis, and has since been described from two Finnish, one Bavarian and one central African pegmatites. The writer now reports its first known occurrence in the United States.

At the Green pegmatite, 3 miles northeast of Pringle, South Dakota, near the south end of the Black Hills, on August 30, 1942, a nearly black phosphate nodule was found in the wall on the north side of the entrance to the tunnel. The material showing a faint greenish tinge, was hard, dense, fine-grained and apparently fresh and unaltered. The nodule was an irregular but smooth-surfaced ellipsoid with major axis horizontal and a foot long, minor axis vertical and half this amount. Its upper surface was in smooth curving contact with perthitic pink microcline; otherwise it was surrounded by albite-quartz-muscovite-tourmaline rock; columbite plates (as well as muscovite sheaves) in the latter rock extended into the phosphate nodule in typically-striking euhedral cross-cutting relationship. There was a hint of rectangular cleavages here and there in the phosphate; its other physical properties are as follows: Hard. 5⁻; Fus. 3⁻; streak, brownish; color, greenish-black. Its specific gravity is 3.52, whereas that from Chanteloube is 3.584.

The phosphate nodules of the Black Hills pegmatites, including lithiophilite and montebrasite, apparently form as a rule at an early stage; they are often closely associated with cassiterite, and in many instances have suffered partial replacement by cleavelandite-columbite rock. Under the latter circumstances the Fe-Mn phosphates not uncommonly show evidence of some oxidation which apparently occurred through hydrothermal action. Mason and Quensel have demonstrated that the Fe''-Mn'' phosphates suffer oxidation in two stages, first the iron,

then the manganese. In many cases these nodules, which may be several feet across are composed in the main of single crystals, as is shown by their cleavages. Whether these crystals grew without the development of faces, or they later underwent partial solution, is a moot question. Rarely the smaller masses are subhedral, but in general these phosphates are low in the writer's morphogenetic series. It may seem unreasonable to think that essentially all of the larger crystals have suffered corrosion, but the Fe-Mn phosphates are very sensitive to oxidation.

X-RAY EXAMINATION

Precession pictures were taken of samples from La Vilate quarry near Chanteloube, Haute Vienne, France, and the Buranga pegmatite (lat. $1^{\circ}48'$ S., long. $29^{\circ}40'$ E.) in Ruanda, Central Africa (Thoreau, 1954). These were in good agreement, but the better results were obtained from the Buranga material. The crystals were monoclinic.

	<i>a</i>	<i>b</i>	<i>c</i>	<i>B</i>
Buranga—	$12.004 \pm .002$	$12.533 \pm .004$	$6.404 \pm .001$	$114^{\circ}22' \pm 05'$
Chanteloube	$11.99 \pm .02$	$12.44 \pm .04$	$6.38 \pm .02$	$114^{\circ}20' \pm 10'$

The diffraction symbol is $1\ 2/m\ 1\ C \cdot c$; the conditions limiting the possible reflections are

$$hkl: h + k = 2n$$

$$h0l: l = 2n; (h = 2n)$$

$$0k0: (k = 2n)$$

The space group is thus $8-Cc=C_s^4$ or $15-C2/c=C_{2h}^6$, probably the latter.

Solely from the point of view of lattice geometry the elements could be $a:b:c = 11.02:12.52:6.38$ with $\beta = 97^{\circ}40'$. This is a less oblique cell, but yields systematic absent spectra which do not fit space group criteria. The transformation formula from this cell to the true one is $101/0\bar{1}0/00\bar{1}$.

Powder films were taken of alluaudite from several localities; the measurements are given in Table 1, and copies of four of them appear in Fig. 1. The Guinier-Wolff (Nonius) camera results, No. 4 in Table 1, are considered to be most accurate, since the dispersion of this instrument is equivalent to what would be obtained from an ordinary 229 mm. powder camera. Of course the number of lines shown in Table 1 depends on the dispersion of the camera. Using a standard 114 mm. camera, alluaudite is well characterized by the following six lines:

$$\frac{2.73/10}{12 \text{ (also 13?)}}, \quad \frac{6.27/8-}{2}, \quad \frac{3.07/7}{7-9}, \quad \frac{2.51/7-}{17}, \quad \frac{5.47/6-}{3}, \quad \frac{3.49/6-}{5}.$$

The symbol is: (spacing/intensity)/(line number), where relative in-

TABLE 1. SPACINGS AND INTENSITIES FROM ALLUAUDITE POWDER FILMS

Line No.	Indices*	Computed† spacings	1 Pringle		2 Sukla		3		4		5		6	7 Varuträsk
			Chanteloube		Buranga		Chanteloube		Buranga					
1	110	8.19	3	8.241	1½	8.181†	3	8.181†	2+	8.3890	2	8.25	8.13	8.325
2	020	6.266	8	6.296	8	6.279	8	6.261†	8	6.3680	7	6.25	6.271	6.246
3	111	5.67	6	5.470	6	5.470	6	5.470†	4	5.5247	5	5.45	5.458	5.363
—	200	5.468	—	—	—	—	½	4.880†	—	—	—	4.90	—	—
—	021?	4.299	—	—	—	—	½	4.640†	—	—	—	4.65	—	—
4a, b	111, 220	4.182, 4.142	3	4.119†	1½	4.157†	2	4.119†	2	4.2101	1	4.33	4.100	—
—	221?, 311	3.99, 3.708	—	—	—	—	—	—	—	4.1522	—	4.12	—	—
5	310, 131	3.49	5	3.493	5	3.509	6	3.482†	7	3.5145	5	3.49	3.471	3.471
—	202?	3.18	1	3.351	—	—	—	—	—	—	—	3.31	—	—
6a	040	3.133	1	3.204	1	3.139§	7	3.053†	1	3.2049	8	3.11	3.042	3.051
6b	112	3.072	5	3.053	5	3.081§	—	—	5	3.1625	—	3.05	—	—
7	—	—	—	—	—	—	—	—	—	3.0857	—	—	—	—
8	131	3.047	—	—	—	—	—	—	—	3.0551	—	—	—	—
9	221	2.964	—	—	—	—	—	—	—	2.9673	—	—	—	—
10	002	2.9168	—	—	—	—	—	—	—	2.9312	—	—	—	—
11a	312	2.868	1	2.909	1	2.934	1	2.888	2	2.8883	—	2.90	—	—
11b	331, 222	2.849, 2.836	3	2.860†	1	2.853§	2+	2.860	1	2.8504	1½	2.85	2.851	2.871
11c	041	2.760	3	2.819†§	—	—	1	2.819	1	2.7744	—	2.81	—	—
12a	330, 400	2.745, 2.734	10	2.715	10	2.737†	10	2.715†	7	2.7431	10	2.71	2.706	2.706
12b	240	2.715	2	2.643†	1	2.667	1	2.643	10	2.7328§	—	—	—	—
13	(421), 241	2.696, 2.680	2	2.643†	1	2.614	1	2.643	10	2.7057	—	—	—	—
14	022	2.647	2	2.643†	1	2.614	1	2.643	1	2.6534	—	—	—	—
15	402	2.600	—	—	—	—	—	—	1	2.6124	—	2.63	2.617	—
—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
16	311	2.583	2	2.586†	6	2.537	1	2.591	½	2.5941	—	2.578	2.58	—
17a	132?	2.525	4	2.510†	—	—	6	2.510†	3	2.5344	—	—	—	—
17b	112, 420	2.517, 2.500	4	2.510†	—	—	—	6	2	2.5171	6	2.50	2.496	2.509
—	150	2.443	1	2.396†	½	2.415	—	1	2	2.5171	—	2.39	—	—
18	332?	2.408	1	2.396†	—	—	—	1	½	2.4183	—	—	—	—
—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
19	422, (511), 151	2.396-2.332	1	2.336	1	2.349	1	2.327	1	2.3495	—	2.32	—	—
20	(241), 331, (242)? (202)	2.290-2.225	—	—	1	2.246	1	2.226	1	2.2395	—	2.22	—	—
21	(512), (332), (351)	2.210-2.183	3	2.145	½	2.204	1	2.182	3	2.1938	—	2.18	—	—
22	(512), (441), 510	2.160, 2.151	—	—	2	2.169	2	2.148	2	2.1624	1	2.15	2.145	2.146
23	042?, (351), (222)	2.135-2.096	—	—	—	—	—	—	2	2.1361	—	—	—	—

Line No.	Indices*	Computed† spacings	1 Pringle		2 Sukula		3		4		5		6	7 Varuträsk		
									Chanteloube		Buranga					
24a	060, 313̄, (531)	2.089-2.078	4	2.084	3	2.108	4	2.084	2	2.0759	3	2.08	2.079	2.085		
24b	350, 440, (421), (113)	2.064-2.033	3	2.063§	2	2.079§	1	2.060§	1	2.0481§		2.06				
—	223̄, 442̄	2.015-1.998														
25a	532̄, (152?)̄, (061)	1.980-1.966	3	1.952	3	1.961†	1	1.982†	1	1.9432		1.975				
25b	(261̄), 260, 602̄	1.951-1.944	3	1.931§	1	1.923	2	1.949				1.94				
—	(261̄), 530, 423̄	1.937-1.929					2	1.934§				1.93§	1.938			
26	352?̄, (312)	1.908, 1.902	1	1.897†			3	1.903†	3	1.9186		1.90				
27	621̄, 333̄	1.886					3									
28	(513̄), (023), 622̄	1.869-1.853	1	1.854	1	1.871	1	1.859	1	1.8702						
—	(133̄), (600), 351	1.848-1.813	1	1.838§	2	1.833			1	1.8254						
—	242?	1.813	2	1.818			2	1.818								
29	511, 152?	1.795-1.793	2	1.793	2	1.808	2	1.793	1	1.8006						
30a	113, 441, 261	1.775-1.773														
30b	(170), 243?	1.767-1.761	1	1.744†	1	1.779	1	1.764	3	1.7686						
30b	332, (620), (262)?	1.748-1.746	2	1.721	3	1.761§	2	1.744	1	1.7519			1.743			
31	(551̄), 171, (533)?	1.730-1.722	1		2	1.738	1	1.723	2	1.7317						
—	461̄, 443?̄, 062?	1.711-1.700					3	1.678†								
32	402, 712, 711	1.680-1.674	2	1.648	2	1.664†	2	1.656	1	1.6631			1.649			
—	641̄, 552̄, 623̄, 531, 043?	1.674-1.660														
—	133, 642̄, 460	1.649-1.647														
33	550, (462̄), (371̄), 422̄	1.646-1.622	1	1.621†	1	1.634	1	1.619	3	1.6226			1.611			
34a	(353̄)?̄, 370	1.616-1.607	1	1.598†	2	1.594†	3	1.595	1	1.5996						
34b	314, 153?̄, 404	1.593-1.592	1	1.593§												
35	204, 223, 640, 080	1.587-1.5667	3	1.575†			5	1.579†	2—	1.5824†	3	1.575	1.574			
36			1	1.546	2	1.545	1	1.549								
37			2	1.529	2	1.526	2	1.533								
38			1	1.515	1	1.509	2	1.517								
39			1	1.492†	3	1.483	2	1.498								
40			2	1.468			2	1.471								
—							1	1.459								
41			1	1.450†	2	1.432†	1	1.448								
42			1	1.415†	2	1.409†	2	1.418								
—				1.384†												

* Indices in parentheses are regarded as unlikely ones.

† Spacings (non-pinacoidal) computed graphically, using Peacock-Bloss technique.

‡ Diffuse line.

§ Doubler (with the line immediately above).

Nos. 1, 2, and 3 taken on Straumanns (Philips) 114 mm. camera with Fe/Mn radiation; spacings and intensities by Leon Atlas; back-reflection lines (none very strong) omitted.

No. 4 taken on Guinier-Wolf (Nomus) multiple camera with monochromatized cobalt radiation.

No. 5 taken like numbers 1-3, but spacings by D. J. F. using a Nies scale; all intensities not given are <1; 10 weak lines between 1.90 and 1.575 omitted.

Nos. 6 and 7 computed from results by Thoreau.

tensities are on a 10 unit scale. The indices of the lines involved can be obtained from the line number, using Table 1.

The relative intensities of the diffracted spots from all but 19 of the planes listed in the second column of Table 1 were observed on single crystal pictures. Those not seen include 021 , $22\bar{1}$, $13\bar{2}$, $33\bar{2}$, $24\bar{2}$, 132 , 042 and 12 others (all with $d < 2.0$) indicated by a question mark (?) in the table. There was good agreement between observed intensities on the single crystal photos and those on the powder films except as follows: $(20\bar{2})$ no. 6a is very weak on single crystal pictures; $(53\bar{2})$ just above No. 25a is very strong on single crystal pictures; $(33\bar{3})$ just above No. 27 has intensity 3 on single crystal pictures; while (133) and $(64\bar{2})$ just above No. 33 have intensities of 3 and 9 on single crystal pictures. It is possible that numbers should be assigned to the lines just above Nos. 25a and 33.

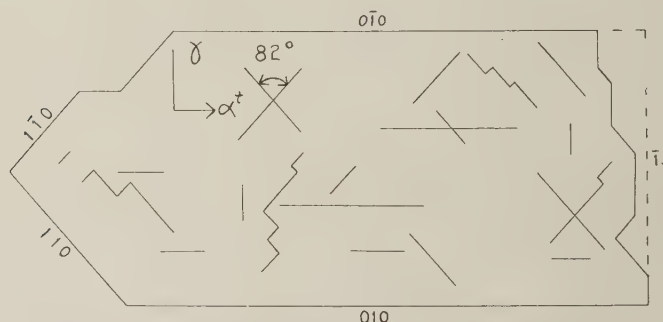


FIG. 2. Sketch of $(\bar{1}01)$ cleavage flake of alluaudite, modified slightly from J. Thoreau. α is $10^\circ.75$ off the plane of the section, dipping "down" in the direction of the arrow. The (100) plane makes an angle of about $82\frac{1}{2}^\circ$ with the plane of the section; the angle is about $84\frac{1}{2}^\circ$ for the $\{110\}$ planes.

OPTICAL PROPERTIES

The $(\bar{1}01)$ cleavage flake of Buranga alluaudite, still on the same goniometer head with $[a^*]$ parallel its axis used for taking the x-ray precession pictures, was mounted on the universal microscope-goniometer (Fisher, 1952). Using the latter as a one-circle optical goniometer, it was determined that the S -arc had to be moved through $7^\circ.39$ to bring the $(\bar{1}01)$ cleavage (which was substantially parallel to the L -arc) parallel the dial axis. Using the instrument as a microscope with the crystal projecting into a cell containing methylene iodide, it was found that the S -arc had to be moved through an additional $10^\circ.75$ to bring an indicatrix axis (α) parallel to the dial axis. It was thus shown that $\alpha \wedge [a^*] = 18^\circ.14$; or that $\beta \wedge [c] = +18^\circ.14$ (with β lying in angle μ or "acute angle β ") since $[b] \sim \gamma$. Figure 2 shows J. Thoreau's sketch, slightly modified, with the addition of indices.

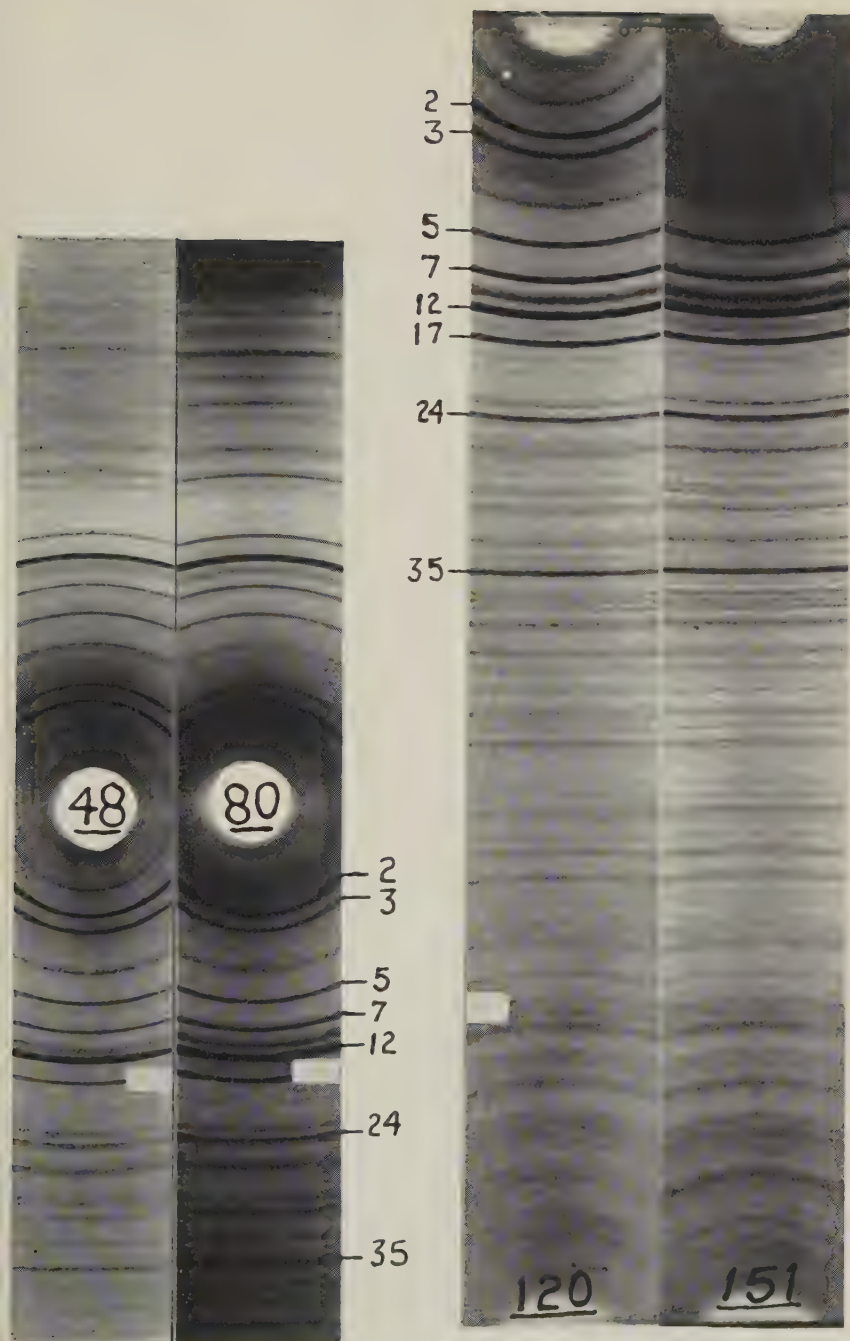


FIG. 1. Alluaudite powder films; left to right: Pringle, Sukula, Chanteloube, Buranga. All taken with Fe/Mn radiation in a 114 mm. Straumanis (Philips) camera. The two on the left are reduced; the others are approximately natural size. Some of the lines are numbered to correspond with what is given in the first column of Table 1.

The attempt to measure α was unsuccessful since its value appears to be above that of my 1.78 oil (*S* in methylene iodide) which at the temperature examined has indices 1.7887 (*E*-line) or 1.7747 (*D*-line). Even at $\lambda = 500\text{m}\mu$ ($n = 1.7966$) α of alluaudite seemed to be higher than the oil. I believe that the approximate value of α of 1.77 given by Thoreau is somewhat low. The higher $-n$ oils at my disposal contain phenyldiiodoarsine or arsenic tribromide; even the latter is not very transparent when used in the thinnest ($1/16''$) cell of my instrument, and the results obtained could not be interpreted satisfactorily.

In determining the birefringence $\gamma - \alpha$ of the crystal, the thickness of the cleavage flake was found to be 0.03340 mm. (in a direction $10\frac{3}{4}^\circ$ off the normal), and between crossed polars at 45° the retardations R observed are shown in Table 2. That is, for $\lambda = 630$, the retardation was just 3λ ; for $\lambda = 533$, it was just 4λ ; and in white light it was estimated that R

TABLE 2. BIREFRINGENCE ($\gamma - \alpha$) OF ALLUAUDITE

No.	λ	R	$R/t = \gamma - \alpha$
3	630	1890	0.0567
—	white	2000	0.0599
(3.454)	579	2000	0.0599
4	533	2132	0.0638

was 2000, using the Michel-Lévy birefringence chart; this corresponds to the data in line 3 of the table. It is considered that the birefringence values given for $\lambda = 630$ and 533 are accurate within a few units in the fourth place. In short this technique leads to a quite accurate determination of the dispersion of the birefringence.

It was impossible to observe $\beta - \alpha$, since one is then looking nearly parallel the cleavage flake and the thickness is thus so great that the crystal is opaque. When looking at the $\gamma\alpha$ section the thin edges show the color for α as light brown, that for γ dark brown; i.e., $\text{Abs.}_\gamma \gg \text{Abs.}_\alpha$.

Working with crushed grains embedded in immersion media and using a sodium light Mrs. Phyllis Hull determined the indices of refraction of the Pringle alluaudite to be $\alpha = 1.782 \pm .005$; $\beta = 1.802 \pm .002$ and $\gamma = 1.835 \pm .01$. Its color varies from pale olive (α) to medium olive (γ).

Study of a thin-section of the Buranga alluaudite on the universal stage (1.649 segments) using white, Na-vapor, and filtered Hg-vapor ($\lambda = 546\text{ m}\mu$) light, yielded the following results. $\text{Abs.}_\gamma = \text{Abs.}_\beta > \text{Abs.}_\alpha$; the colors are: $\alpha \rightarrow$ straw to greenish-yellow straw; and $\beta = \gamma \rightarrow$ light yellow green to pale olive greenish to brownish-yellow. These observations were made on three different crystals using a micro-dichroscope; of course the

deeper shades refer to conditions where the thickness of the section was greater, due to higher tilt angles. The material is optically positive with $2V_{Na}=79.^{\circ}2$ and $2V_{Hg}=78.^{\circ}0$; i.e., crossed dispersion $r > v$, moderate. Thus since $\gamma - \alpha = 0.060$, it follows that $\gamma - \beta = .035$ and $\beta - \alpha = .025$. Crystals observed looking approximately along $[b] \rightarrow \gamma$ show thin polysynthetic twin lamellae with (101) the composition plane. The latter is a plane of symmetry between the two parts of the twin, since when it is set normal to the A_4 -axis (and parallel the vibration direction of the polarizer) the twin lamellae and the main part of the crystal show the same interference color, no matter what the A_4 reading. The absence of extinction between crossed polars when looking along an optic axis is very pronounced. This made orientation of the optic plane by standard extinction procedure quite difficult. This was remedied by using the isogyres for orientation purposes as follows: after getting approximate orientation by standard procedures and rotating on A_4 (conoscopic observation; polars at 45°) till a melatope is at the center of the field with an isogyre approximately parallel to A_4 , the stage is rotated 45° on A_5 making the isogyre about normal to A_4 ; it is brought normal to A_4 by rotation on A_1 and made to go through the center of the field by tilting on A_2 . Repetition of this procedure once or twice results in very perfect orientation of the optic plane. It should be noted that the absence of extinction along an optic axis is not due to dispersion (even in monochromatic light there is no extinction) but is caused by conical refraction (there is no evidence of rotary polarization); the conical angle for alluaudite is about $1^\circ 53'$.

CHEMICAL COMPOSITION

The results of recent analyses of alluaudites appear in Table 3. It will be noted that these samples are much closer to the iron-end of the Fe-Mn series than is true for any previously-described samples. Thus the Fe/Mn ratio is 1.07 (Sukula), 1.76 (Buranga), and 2.29 (Pringle); all other described samples are mangan-alluaudites. The original alluaudite carries slightly more manganese than iron ($Fe/Mn=0.96$). Nevertheless Dana's System (II, 674, 1951) has followed Quensel (1937) in using the terms alluaudite and mangan-alluaudite rather than alluaudite and ferri-alluaudite as would seem more logical. Spectrographic examination of the Green Mine alluaudite by Oiva Joensuu showed traces of Al, Ti, and Cu; and absence of Li, Co, Ni, Zr, Zn, Cd, Ag, Mo, V, Bi, Ge, Ga, W, Cr, and Pb. Recent work (Fisher, 1955) has stated that ferrodickinsonite (arrojadite) alters to alluaudite when heated between 485 and 555° C. It thus follows that the two must have related formulas, in which water is considered to play no essential role. This matter will be discussed

TABLE 3. RECENT ANALYSES OF ALLUAUDITES

	1	2
Li ₂ O	—	0.09
K ₂ O	0.02	—
Na ₂ O	4.4	3.90
CaO	4.04	1.40
MgO	0.40	0.47
FeO	1.61	—
MnO	12.9	15.34
Fe ₂ O ₃	30.9	31.48
Mn ₂ O ₃	—	0.88
P ₂ O ₅	43. ±	42.15
H ₂ O+	1.9	} 3.55
H ₂ O—	0.05	
Insol.	1.12	0.58
Total	100.34 ±	99.84

1. Green Mine near Pringle, S. Dak. Analysis by Brynjolf Bruun.

2. Buranga, Ruanda from Thoreau (1954). Other known analyses appear in Dana's System 2 (1951) 674.

in detail in a paper on dickinsonite now nearly ready for submission for publication.

THERMAL PROPERTIES

Heated in air for 24 hours Chanteloube alluaudite melts at about 1000°C.; the air-quenched sample failed to give an alluaudite powder diffraction pattern. Quenched from 990°, although the sample showed strong sintering, it yielded a perfect alluaudite diffraction film. The 960° sample showed only very slight sintering. Professor Thoreau* informs me that the 700° fusion figure given in his paper for the Buranga alluaudite was a typographical error; it should have been 850/860°. His statement regarding the absence of *D.T.A.* phenomena in alluaudite referred only to higher temperatures; he says there is a pronounced endothermal break at 215° C. due to loss of water (Thoreau and Bastien, 1954).

ACKNOWLEDGMENTS

Besides previous credits the writer thanks Dr. Brian Mason for samples from Sukula and Varuträsk, Dr. J. Thoreau for a fine Buranga sample, and Dr. F. A. Bannister for the Chanteloube specimen (British Museum 89941).

* Personal communication (11 Febr. 55).

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THE ENDELLITE-HALLOYSITE NOMENCLATURE*

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ABSTRACT

The nomenclature of the minerals halloysite and endellite is reviewed, and the justification for the continued use of the names halloysite, $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$, and endellite, $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot 2\text{H}_2\text{O}$, is given.

INTRODUCTION

Recent advances in understanding the mineralogy of clays have quite naturally brought some conflicts in nomenclature. Such a conflict has existed since 1935 for two clay minerals that previously had been considered to be the single mineral, halloysite. In an attempt to resolve this difficulty, Alexander, Faust, Hendricks, Insley, and McMurdie (1943) suggested that the name halloysite be restricted to the mineral of composition $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ and proposed the new name endellite for the more highly hydrated related mineral, $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot 2\text{H}_2\text{O}$. The validity of this nomenclature, however, has been questioned by MacEwan (1947). In this paper justification for the continued use of the names halloysite and endellite is more fully developed.

The various suggestions made to date are summarized below:

Author	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot 2\text{H}_2\text{O}$
{ All authors, 1826-1934 }	{ —Halloysite— (treated as a single species) }	
Ross and Kerr (1934)	Halloysite	Not recognized
Hofmann, Endell, and Wilm (1934)	Kaolinite	Halloysite
Mehmel (1935)	Metahalloysite	Halloysite
Hendricks (1938)	Halloysite	Hydrated halloysite
Alexander, Faust, Hendricks, et al. (1943)	Halloysite	Endellite
MacEwan (1947)	{ —Halloysite— (to be used as a group name) Metahalloysite Hydrated halloysite also "partly hydrated halloysite"	
Brindley, G. W. and others (1951)	{ —Halloysite— (Non-specific term for all forms of the mineral)	

HISTORICAL SUMMARY

(a) 1826-1934.

Berthier (1826) gave the name halloysite to a clay mineral from Angleur, Liège, Belgium. The pertinent observations¹ on the water in the

* Publication authorized by the Director, U. S. Geological Survey.

¹ Translated by G. T. Faust.

mineral are given below:

- p. 332. "If powdered halloysite is exposed for a certain time to a temperature near
 p. 333. 100° C., it loses water; beyond that it loses no more than 0.16 by calcination.
 The powder from the drying, but not the calcination, absorbs water rapidly
 if it is dipped into water, or if it is left in contact with humid air."
 p. 333. "If one considered the water which remains after drying in the oven to be
 combined water, the analysis will show:

$$\begin{array}{r} \text{SiO}_2 = 0.4494 \\ \text{Al}_2\text{O}_3 = 0.3906 \\ \text{H}_2\text{O} = 0.1600 \\ \hline \end{array}$$

1.0000

- p. 333. "Indeed, it appears extremely difficult to determine with complete exactitude
 the portion of water which is in a combined state and that which is only ab-
 sorbed by capillary attraction."
 p. 334. "It is very probable that the true composition of halloysite is represented by
 the formula $2\text{AlS}^2 + \text{AlAQ}^2$ which corresponds to the following numbers:

$$\begin{array}{r} \text{SiO}_2 \dots\dots\dots 0.470 \\ 0.393 \left\{ \begin{array}{l} \text{Al}_2\text{O}_3 \dots\dots\dots 0.262 \\ \text{Al}_2\text{O}_3 \dots\dots\dots 0.131 \\ \text{H}_2\text{O} \dots\dots\dots 0.137 \end{array} \right\} \begin{array}{l} 0.732 \\ 0.268 \end{array} \end{array}$$

These statements indicate that Berthier considered the halloysite mineral from Angleur to have the composition $2\text{AlS}^2 + \text{AlAQ}^2$, which in present day usage is $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$, with excess water present as "absorbed capillary water" and not as a hydrate.

Berthier's view that the excess water in the mineral that he examined was not essential, but was rather held mechanically by adsorption or through capillarity continued to be generally accepted, as was natural for this period. Le Chatelier (1887) referred to the excess water as "Eau hygrometrique" (hygroscopic water) and he was followed in this by Lacroix (1893). Le Chatelier (1887) states¹ in addition:

"The water is very sharply divided into two parts—the one part goes off at 150° C. after 24 hours of heating, or at 250° C. in one quarter of an hour; the other part begins to go off only at about 400° C. The proportions of this latter water is always very exactly two equivalents of water to one equivalent of alumina."

Dana (1892) also follows Le Chatelier and writes concerning "halloysite:"

"A silicate of aluminum, like kaolinite, but amorphous and containing more water; the amount is somewhat uncertain but, as shown by Le Chatelier, the formula is probably to be taken as $\text{H}_4\text{Al}_2\text{Si}_2\text{O}_9 + \text{Aq}$, or $2\text{H}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 + \text{Aq}$."

Larsen and Wherry (1917)² studied the dehydration of "halloysite" and the change in the optical properties of the mineral with loss of water. Their conclusions follow:

"Obviously, the water in halloysite is in part only mechanically held. This part is given off very readily and the resulting partially dehydrated material has a composition near that of kaolinite. The formula should therefore probably be written $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O} \cdot \text{Aq.}$

"The close approach of this and many other analyses of halloysite to the composition $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O} \cdot \text{Aq.}$ combined with the results of optical examination given above, indicates that the material called halloysite is the amorphous mineral corresponding to crystalline kaolinite, holding through capillarity or adsorption more or less excess water."

Larsen and Wherry (1917) found that material from Wagon Wheel Gap, Colorado, had an index of refraction of 1.470 ± 0.010 two months after it was collected. This material they regarded as halloysite with unessential water. They found that when this mineral was dehydrated at 65°C. for four hours, its index of refraction rose to 1.555 ± 0.003 .

In the first edition of Larsen's Tables (1921) he lists the following data for "halloysite."

<i>Page</i>	<i>N</i>	<i>Formula</i>
172	$1.470 \pm$	$\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot n\text{H}_2\text{O}$
173	$1.52 \pm$	$\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 + n\text{H}_2\text{O}$
174	$1.542 \pm$	$\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot n\text{H}_2\text{O}$
174	$1.555 \pm$	$\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$

It is clear from the foregoing that the general opinion was that stated in Dana-Ford (1932); "It is probable that halloysite is an amorphous mineral corresponding to kaolin, but holding by capillarity or adsorption varying amounts of excess water." It is then evident that various investigators have observed the hydrated material without recognizing that it was a distinct mineral. It is obvious, however, that all of them considered that the name "halloysite" should apply to the dehydrated form, that is to $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$. MacEwan (1947) has shown that many of the analyses of "halloysite" made before 1934 were probably made on the more highly hydrated material we now call endellite, or on mixtures of endellite and halloysite. It is now known that sub-microscopically crystalline kaolinite has been mistaken for halloysite. This in itself shows that the $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ formula was commonly believed to represent halloysite.

The important point is that prior to 1934 the water content in excess of $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$, was universally considered to be nonessential

² MacEwan (1947) on page 40 states that "Larsen and Wherry in their paper put forward the formula $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O} + 2\text{Aq.}$ " but no such proposal is to be found in their paper. They merely compared their analysis of the mineral with a hypothetical formula of that composition.

water. Mineralogists actually used the term halloysite to refer indiscriminately to $\text{Al}_2\text{Si}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$, $\text{Al}_2\text{Si}_2\text{O}_7 \cdot 4\text{H}_2\text{O}$, and to mixtures of the two, but considered that they were referring to $\text{Al}_2\text{Si}_2\text{O}_7 \cdot 2\text{H}_2\text{O} + n\text{H}_2\text{O}$ (unessential). This was true not only of American mineralogists (see quotation from Dana-Ford above), but also of British and German mineralogists. For example, Read (1936) gives, "Halloysite—Hydrated aluminum silicate, near kaolinite, $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$," and Ramdohr (1936) gives, "Halloysite, $\text{H}_4\text{Al}_2\text{Si}_2\text{O}_9 + \text{Aq.}$ "

I, therefore, believe that application of the term halloysite to $\text{Al}_2\text{Si}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ is in accord with past usage.

(b) 1934—present.

Halloysite was first definitely differentiated from kaolinite by Ross and Kerr (1934), who made chemical, optical, x-ray, and dehydration studies. The form of the dehydration curves and the ease with which water was lost led them to state, "It is quite evident that the water lost up to 110° (1.44 to 4.75 per cent) is not significant, but represents adsorbed water. In fact, the water lost up to 200° (2.5 to 5.20 per cent) is no doubt adsorbed." This study justified them in following generally accepted and long-established usage by applying the name halloysite to the microcrystalline compound $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$.

Spencer (1935) in his abstract of the paper by Ross and Kerr (1934) writes:

"Twelve analyses of halloysite (including 'indianite,' 'newtonite,' and 'lithomarge') from various localities show a $\text{SiO}_2:\text{Al}_2\text{O}_3$ ratio ranging from 206:100 to 165:100, the agreement with the usually accepted formula $\text{H}_2\text{Al}_2\text{Si}_2\text{O}_8$ being only approximate."

This formula given by Spencer may also be expressed as $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot \text{H}_2\text{O}$. This formula does not agree with the analyses in the literature, and has not been accepted by mineralogists.

Hofmann, Endell and Wilm (1934) were the first to show that the x-ray pattern of the fully hydrated mineral differed from that of material heated to 50° or dried over H_2SO_4 or P_2O_5 . They erroneously concluded that the dehydrated material was kaolinite. This may have influenced them to use the name halloysite for the fully hydrated material which they state to be approximately $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 4\text{H}_2\text{O}$.

Mehmel (1936) confirmed their findings that the fully hydrated mineral was distinct (characteristic x-ray line at 10.1 \AA), but showed by optical and x-ray study that the dehydrated material (characteristic x-ray line at 7.46 \AA) was not kaolinite. Mehmel does not give the basis for his nomenclature. Perhaps following Hofmann, Endell, and Wilm (1934), he called the fully hydrated mineral halloysite and referred without comment to the dehydrated mineral as metahalloysite.

The work of Ross and Kerr (1934) was apparently not known to Mehmél when he proposed the name metahalloysite for the same mineral that they had characterized so completely and named halloysite. It is clear that their name has priority over his, which is in itself sufficient basis for dropping the name "metahalloysite." We believe that the historical summary above disproves MacEwan's statement, "Hofmann and co-workers, and Mehmél, were historically correct in assuming that the hydrated halloysite was the true halloysite . . ." Furthermore, MacEwan (1947, p. 36) has pointed out that it is not clear whether Mehmél knew that his "metahalloysite" occurred naturally, all of Mehmél's samples having been prepared by dehydration. Mehmél used the name metahalloysite only in reference to an artificial product, and a name having such a basis has no standing in the nomenclature of mineralogy. The discoverer of the natural mineral may accept, if he wishes, the name applied to the artificial compound, but he is not bound to do so.

For all these reasons, the term *metahalloysite* should be dropped from mineralogical nomenclature.

Hendricks (1938) used halloysite for $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ and hydrated halloysite for $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 4\text{H}_2\text{O}$. He writes, "The great ease with which this dehydration takes place has not generally been recognized and as a consequence there is some confusion in the literature, but as a rule Mehmél's "metahalloysite is the usual halloysite of others." MacEwan questions the validity of this statement, and remarks that no references were cited to support it. The detailed historical summary above warrants our having felt in 1938 that the statement was so much in accord with accepted usage that it needed no defense.

Edelman and Favejee (1940) objected to the terminology of Hendricks (1938) on the basis that this nomenclature gives the erroneous impression that the mineral rich in water originates from the mineral poor in water. The objection is valid, and Alexander, Faust, Hendricks, Insley and McMurdie (1943) proposed the name endellite for $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 4\text{H}_2\text{O}$ and retained the name halloysite for $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$.

To summarize,

- (1) The use of the name halloysite for $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ is consistent with the usage generally accepted over a long period of years;
- (2) The mineral of this composition was first adequately characterized by Ross and Kerr, who called it halloysite;
- (3) The name metahalloysite for the mineral of this composition should be dropped, from consideration of priority, and for other valid reasons.

There remain to be discussed MacEwan's suggestion of the use of halloysite as a group name and his objections to the name endellite for $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 4\text{H}_2\text{O}$.

USE OF HALLOYSITE AS A GROUP NAME

MacEwan (1947) states, "thus the name 'halloysite' would be taken to cover all the naturally occurring halloysite minerals (hydrated, non-hydrated, and intermediate) as well as artificially produced complexes; and for particular forms the precise terms 'hydrated halloysite,' 'glycerol-halloysite,' etc. would be used. . . ." In essence, MacEwan proposes to return to the practice, used before the distinction between the two hydrates was known, of grouping them together under a single term, together with artificial organic complexes.

His justification for this is chiefly his belief "*that the two halloysite minerals are only two members of a series of substances which includes various intermediate forms, . . .*" (Italics G.T.F.), and "I wish to suggest that recent research has shown that halloysite and metahalloysite (hydrated halloysite and halloysite; or endellite and halloysite) are so closely connected that they are more conveniently regarded as two aspects of a single substance than as entirely separate substances."

The weight of evidence seems to point almost certainly to a discontinuity in the series. Such a discontinuity appears in the optical work by Mehmel (1937) and by Alexander, Faust, Hendricks, *et al.* (1943), and in the dehydration studies by Hofmann, Endell and Wilm (1934) and by Mehmel (1937). Optical work at the U. S. Geological Survey is also in agreement with this earlier work.

Brindley and Goodyear (1948) made an x-ray study of the transition endellite to halloysite (halloysite to metahalloysite in their terminology). They found that endellite showed spacings of 9.5 to 10.1 Å, and halloysite 7.5 to 7.9 Å, but were "unable to obtain evidence for the existence of intermediate stages with spacings between 9.5 and 7.9 Å" (p. 411). The variations in spacings found corresponded to variations in the formula $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot n\text{H}_2\text{O}$, with n varying from $3\frac{1}{2}$ to 4 for endellite, $2\frac{1}{3}$ to $2\frac{2}{3}$ for halloysite.

Very convincing evidence for the invalidation of MacEwan's chief argument for the use of halloysite as a group name, quoted above, has come from the recent phase-rule studies on the system $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ and the subsystem $\text{H}_2\text{O-halloysite}$. Bates (1952) has published a diagram delimiting the field of stability of halloysite and endellite as a function of temperature and the vapor pressure of water in the system. He found no evidence of phases intermediate between endellite and halloysite. Roy and Osborn (1954) in their study of the system $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ extended these studies and their comments are especially pertinent to this discussion. On page 861 they write:

"Brindley and Goodyear (1948) have stated that halloysite has an 001 spacing of 7.4 or 7.5kX. Such a spacing was encountered in several of our runs and it was at first consid-

ered feasible that the 7.4 Å reflection—characteristic of a hydrate with more than 2 H₂O—represented the true value for halloysite. This would have meant that halloysite and kaolinite are not polymorphs. However, a study of the spacings of halloysite dehydrated at temperatures from 100° C. to 450° C. shows that after the attainment of equilibrium the spacing is constant at 7.17 Å. Apparently in the work of Brindley (1951, p. 52) and also in our runs which yielded a structure with a 7.4 Å spacing, dehydration was not carried to equilibrium at the temperatures used. In hydrothermal runs at temperatures and pressures in the region near the equilibrium decomposition curve, endellite may dehydrate only partially to yield the 7.4 Å phase. However, we have found that the spacing of halloysite derived by decomposition of endellite under temperature and pressure conditions existing to the right of Curve II (Fig. 6) is invariably 7.17 Å. Moreover, halloysites dehydrated at 110° C., 300° C. and 400° C. would not rehydrate to the 7.4 Å phase, even under high water pressures at appropriate temperatures. While the above shows that halloysite is a true polymorph of kaolinite with a 7.17 Å spacing, it also does suggest that the interlayering proposed by Brindley and Goodyear has some unique stability, since no other intermediate spacings have been consistently found."

MacEwan suggests that there are advantages in the use of "halloysite" as a vague general term but this seems dubious to me. I believe that mineralogic nomenclature should not be burdened by devising mineralogical names for such organic complexes of clay minerals as "glycol-halloysite."

MacEwan (1947) states that the name endellite has no obvious connection with halloysite. This point is really an advantage as there is no ambiguity about the meaning of the name. The name endellite is being used by many mineralogists in the United States, and also is being rapidly adopted by economic geologists. Callaghan (1948) has described the economic geologic relations of endellite in the Gardner Mine Ridge area, of Lawrence County, Indiana.

In Germany the name endellite also is being used by mineralogists. Professor Strunz (1949) is using these names in his *Mineralogische Tabellen*. Professor Ulrich Hofmann in a letter to Dr. Clarence S. Ross³ writes as follows:

"Questions of nomenclature always appear to me as something difficult and I am very grateful to you and Dr. Hendricks that you have undertaken this difficult question so fundamentally. I myself have, as you know, first used the name halloysite for the mineral with the higher water content, 4H₂O·Al₂O₃·2SiO₂ and Mehmel has followed this usage. The essence of this is, as you have already emphasized, what did mineralogists previously understand the name halloysite to mean? If the name halloysite refers to the water-poor mineral 2H₂O·Al₂O₃·2SiO₂, then Endell, Wilm, and I have in our paper, *Angewandte Chemie*, 47, (1934) 541, for the first time recognized correctly the existence of the water-rich mineral. It is accordingly correct to give this new mineral a name and I am very grateful to you, that you have chosen for it the name of my lifelong and unfortunately deceased friend and coworker, Endell."

and in 1955 in a letter to the author⁴ he states:

"My associates and I find the names endellite and halloysite useful and justified."

³ Personal communication, June 26, 1949.

⁴ Personal communication, April 19, 1955.

SUMMARY

For nearly a hundred years, the name halloysite was applied by many mineralogists indiscriminately to both $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ and $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot 2\text{H}_2\text{O}$ in the mistaken belief that the additional water in the more highly hydrated mineral was unessential and adsorbed. Halloysite was never clearly defined or characterized until the work of Ross and Kerr on the whole kaolin group. These authors were clearly justified in following the long accepted usage and restricting the name halloysite to the mineral with only $2\text{H}_2\text{O}$.

The acceptance of the name endellite for the mineral with $4\text{H}_2\text{O}$ will obviate ambiguity and leave no doubt about the identity of the mineral under consideration as the proposal of MacEwan does not do.

Hofmann, who first discovered and described the mineral, has agreed to the name endellite for this mineral with higher water content.

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TECHNIQUES EMPLOYED IN THE IDENTIFICATION OF GEMSTONES*

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The problems attendant to the identification of gemstones would seem to be simple in that only a small number of minerals have gem varieties. Although the number of natural gem minerals is small, the increasing number of synthetics and cleverly contrived imitations plus the limitations imposed by the necessity to return a gemstone to its owner totally undamaged, add to the problems of the person seeking to identify gemstones.

The combination of powder analysis by x-ray and by the petrographic microscope provides for the mineralogist conclusive means of identification. Since the jeweler can neither powder a gemstone nor subject it to chemical analysis, some important mineralogical methods are not applicable to gem identification.

The development of gem identification to an exact science has been rather recent. The first of the three most important gemtesting instruments, the refractometer, was adapted for gemtesting purposes by G. F. Herbert Smith in 1905. Until the gem polariscope was developed in 1935 and the dark-field illuminator for gemstones by Robert M. Shipley, Jr., in 1938, the jeweler was forced to rely heavily on the petrographic microscope. That instrument, designed for thin section or powder work, is quite impractical for the examination of gemstones. Thus, as gemtesting developed, property determinations once made laboriously by the use of the petrographic microscope were obtained by utilizing the refractometer, a simple polariscope employing Polaroid film, and a binocular microscope equipped with a dark-field illuminator.

Originally, the polariscope was used only to distinguish between singly and doubly refractive materials and to test for pleochroism. However, other uses developed rather rapidly. Perhaps the most important is the determination of optic character and sign. This may be a very simple determination or rather awkward, depending on the shape to which the stone is cut, its refractive index and its orientation.

Since a transparent cabochon-cut gemstone acts as its own condenser, a gemstone cut in this rounded form displays an interference figure with-

* The following comments were written in the belief that some of the techniques peculiar to gemstone identification are little known outside that specific field. Much of the material presented here has appeared in books or periodicals in the field of gemology either in Europe or America.

out magnification when examined between crossed Polaroid plates. For example, star sapphire, which must be cut with its axis perpendicular to the girdle plane of the cabochon, shows an interference figure in the polariscope in the same position in which the star appears in reflected light. In a cabochon form of cutting, an optic axis interference figure is visible without magnification in any stone in which an optic axis is more or less tangent to the convex surface. The situation is slightly more complicated with faceted stones but since the shape of a faceted stone generally is roughly spherical or hemispherical, even a faceted stone acts as an inefficient condenser. Thus with magnification, an interference figure may be obtained. In order to do this, the stone, held by the forefinger and thumb, is rotated between crossed Polaroid plates until a brush is observed. The stone is then turned in a plane that will sharpen the brush until interference colors are observed. At that point a lens is inserted between the stone and the upper Polaroid to resolve the figure. For sign, a quartz wedge is employed.

In a faceted stone the orientation of facets with respect to optic axes may be such that a figure is very difficult to resolve. Several rather interesting means of obtaining figures in such cases have been developed over the years. In one, developed by Kenneth M. Moore, a hollow sphere of glass is ground off on one side so that a small bottle top may be cemented to it. Within the neck of the bottle a beeswax holder is mounted under a water-tight rubber cap. The sphere is filled with water and the stone mounted in the beeswax is placed in the water. Then the sphere is rotated between Polaroid plates until interference colors are observed. Magnification in the form of a small lens resolves the figure. In the case of a biaxial stone, the points at which the optic axes are observed are marked in ink or wax pencil on the surface of the glass and the interaxial angle measured roughly.

There are other simple methods to make possible the resolution of an interference figure when interference colors have been located, but the figure has proved difficult to resolve. When a drop of methylene iodide is placed at a point at which colors are seen, the surface tension of the dense liquid causes it to stand up in a drop form. The high refractive index of methylene iodide makes the drop an effective condensing lens. If this proves insufficient, a glass rod with a spherical tip is placed on the methylene iodide and the figure may be seen in the spherical tip.

A student at a class in advanced gemology introduced a clever idea to speed his efforts to obtain figures. He brought to class a jar of very viscous honey, into which he dipped a stone when he had difficulty resolving an interference figure. The honey-coated stone made a more or less spherical mass which behaved as a condensing lens and reduced facet

distortions, facilitating his efforts to obtain interference figures otherwise difficult to resolve. This method works nicely with transparent rough as well as faceted material.

Robert M. Shipley, Jr., took the principle of the Federov stage as the basis for a design of a universal motion immersion stage. In this a stone mounted on wax was attached to a small table which could be rotated on its mount. In turn, the table was mounted in a ring that rotated in one plane while an outer ring also rotated but in a plane at 90° to the plane of motion of the inner ring. Rotation of the rings was controlled



FIG. 1. The illuminator polariscope.

by gears operated by knobs outside the cell. This facilitated both the resolution of optic axis interference figures, and in biaxial stones the measurement of the interaxial angle.

Because of the thickness of the average gemstone, in a biaxial figure only one "eye" is seen at a time and the brush appears to be straight unless the $2V$ angle is very small. The Bx_a direction is determined from the difference in the clarity and sharpness of the interference rings toward and away from that direction.

The polariscope also is used to distinguish between anomalous and true double refraction, which is a difficult determination for the begin-

ner. It is accomplished by first rotating the specimen between crossed Polaroids to the position of maximum light transmission through the stone. While holding the specimen in this position, the analyzer is rotated toward the polarizer vibration direction (in other words, from dark to light). Birefringent material will either darken slightly (possible if pleochroic) or retain the same light intensity. Strained isotropic materials will pass more light as the analyzer is rotated away from the 90° position. This method is effective for most gem materials but may be useless with badly strained isotropic materials—particularly some garnets, amber, and plastics.

Developments in jewel refractometer techniques in recent years have multiplied its utility to the gemologist. For many years it was used almost exclusively to obtain a refractive index figure which could be read easily only to about .01 in white light. Readings were obtained only from fairly broad flat surfaces. Using white light without filters, a reading appears as a single, broad, partial spectrum for gemstones with a birefringence up to about .010 or .012. Although filters or monochromatic light have been employed for many years to sharpen readings, the analysis of optic character on the basis of the behavior of the index readings as the stone is rotated is a more recent practice.

When a stone is being tested on a refractometer hemisphere, the direction analyzed by the instrument is that parallel both to the top surface of the hemisphere and to the long axis of the instrument. In other words, if a prism face of a tetragonal or hexagonal crystal were placed on a hemisphere with its c axis parallel to the long axis of the instrument, a single reading would be evident.

Rotation of the crystal on the hemisphere will bring a second reading into evidence with maximum birefringence reached when the c axis is at 90° to the long axis of the refractometer. If the basal pinacoid of this crystal were placed on the hemisphere, two readings would be seen which would be constant at maximum birefringence during rotation on that facet. On a facet with any other orientation, sign is determined by noting whether the high or low reading is constant. Regardless of orientation, any facet on a uniaxial gemstone will give maximum birefringence upon rotation of the stone on the hemisphere. Only when a facet is perpendicular to the optic axis is it necessary to take a second reading to determine optic sign.

The analysis of birefringence for a biaxial gemstone on a refractometer is only slightly more complicated. For most orientations, the two readings vary as the biaxial gemstone is rotated. For biaxial gemstones, sign is determined by noting whether α or γ varies more or to which β is closer. A rough approximation of the value of $2V$ is made by the rela-

tive position of β index with respect to α and γ . If β is about midway between, $2V$ is near 90° .

On a facet perpendicular to γ (the acute bisectrix in a positive mineral) one reading remains constant at the γ value and the other varies from α to β . On a facet cut perpendicular to α (the obtuse bisectrix in a positive mineral), the α index is constant and the other reading varies from a minimum value of β to a maximum of γ . On a facet parallel to the principal section, β is constant and the other reading varies from α to γ . On facets oriented in other than these directions, α and γ may be determined by noting minimum and maximum readings, but β is more difficult to pinpoint. The sign is obtainable if one of the readings moves across the midpoint between the extremes which represent α and γ values.

At one time many gemologists favored refractometers with rotating hemispheres to facilitate analysis of birefringence. More recently the increased cost attendant to the manufacture of such instruments has caused most gem men to favor refractometers with fixed hemispheres or sections of a hemicylinder.

Since World War II, two refractometers have been manufactured in quantity in the United States, the Erb & Gray and the Gem. Both instruments employ very simple optical systems consisting only of a diffusing screen at the light portal, the dense contact glass, a scale, a means of effecting a change of light path (in one case, a prism and in the other, a first-surface mirror), and a small magnifier. Each employs a movable eyepiece arm which may be removed from the system. It was this latter feature which led Lester B. Benson, Jr., to the discovery of a means by which accurate refractive index readings could be made on curved surfaces as well as facets much too small to give readings by conventional means. Benson noticed that when no magnification was used that the contact between gem and hemisphere appeared as a tiny spot on the scale. By moving the eye back and forth over the scale, and viewing it with lower magnification than that afforded by the eyepiece lens, readings were easily obtained from surfaces on which none was visible otherwise. Curved surfaces reversed the light and dark sides of a reading, but accurate readings could be made with ease. Thus the value of the refractometer in gemtesting increased materially.

In order to make such readings, the amount of contact liquid must be kept to a minimum for accuracy. When the cabochon is resting on the droplet, the spot should not extend over two to three .01 divisions on the scale. As the eye is moved back and forth over the scale, the spot is seen to change abruptly from dark to light. When white light is employed, a blue-green line may separate the light and dark zones at the

reading, but if the spot is tiny, the line of color may not be visible. If no blue-green line is observed, the reading is taken at a point midway between the point at which the spot is last dark and first light as the line of sight moves from the low to the high numbers on the scale.

Magnification of the interior of a gemstone is a very important phase of gemtesting because of the synthetic counterparts of corundum, spinel and the emerald variety of beryl, and the many imitations and



FIG. 2. The "gemolite" with overhead light source.

dyed stones on the market. The rather narrow gap between the melting point at about 2100°C . and boiling point about 100° higher makes synthetic corundum difficult to produce by the Verneuil process without gas bubbles. The presence of gas bubbles and/or curved accumulation lines formed during the growth of the boule prove synthetic origin. In order to examine the interior of a gemstone effectively, careful lighting is essential. Without dark-field illumination, it is all but impossible to detect minute inclusions. As a matter of fact, even large inclusions are undetectable in fairly dark mounted stones under ordinary lighting. When

transparency and lighting permit resolution of the opposite side of a gemstone, a very close approximation of birefringence may be made by an experienced observer. Doubling of facet edges may be seen in a stone of one carat size when the birefringence is as low as .004.

In 1937 an illuminator employing the dark-field principle was first designed for gemstone examination by Robert Shipley, Jr. Binocular-magnification is used for the depth perception it affords and the convenience of upright image, long working distance and large field. Magnifications of $10\times$ to $60\times$ provided by low-powered objectives and high-powered eyepieces are used most effectively in gem identification.

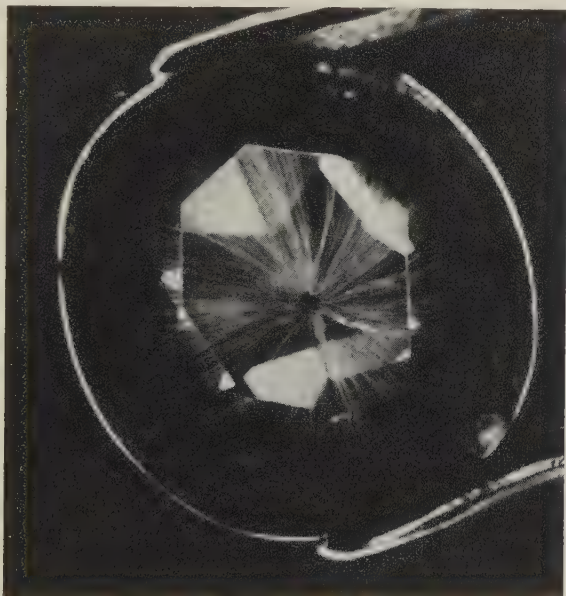


FIG. 3. Radial fibrous inclusions in the demantoid variety of andradite garnet $10\times$.

While few gemstones have inclusions so characteristic as to permit identification beyond question, frequently magnification of the interior will give the experienced individual clues to the identity of a gemstone—and, often leave him morally certain what it is. However, a sight identification based on inclusions, should be confirmed by other tests.

Some very interesting characteristics are sometimes revealed under magnification. For example, emeralds from Colombia and the Urals may be distinguished from one another by the shape of minute tabular crystals found in liquid and gas-filled cavities. In Colombian emeralds the flat crystals are square in outline, while in the Uralian product they are diamond-shaped.

The demantoid variety of andradite garnet almost always contains brown radiating fibers unlike inclusions found in any other gemstone. The hessonite variety of grossularite garnet has a characteristic appearance under magnification which is reminiscent of sugar dissolving in water.

However, the key use of magnification is simply to distinguish the man-made from the natural. In some cases, this is the most difficult problem in gem identification, despite which some jewelers make "identifications" by sight, and some mineralogists "identify" with magnification and lighting equipment totally inadequate for the resolution of essential characteristics.

There are many effective imitations to trap the unwary. Glass imita-

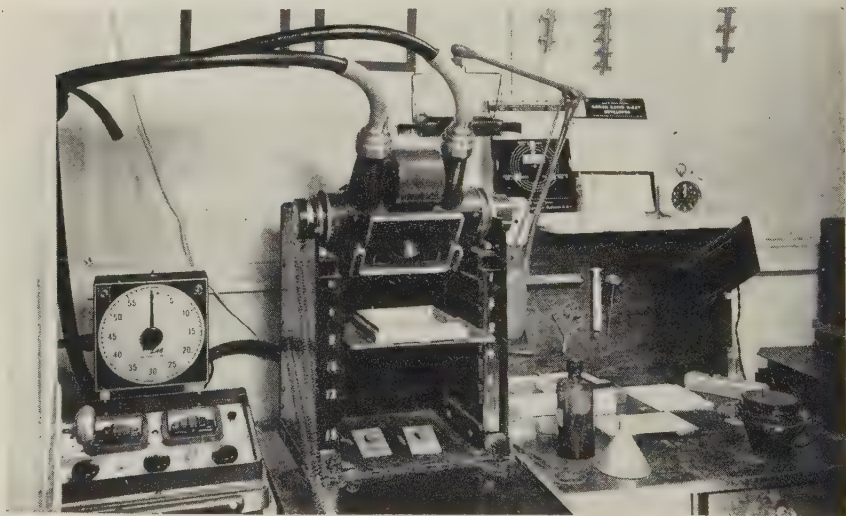


FIG. 4. Pearl radiography equipment utilizing a Picker tube with tungsten target.

tions of turquoise and gem varieties of chalcedony may have refractive indices in the same range and the same specific gravity. However, the vitreous luster on minute conchoidal fractures on glass contrasts with the waxy to dull luster on fracture surfaces of both chalcedony and turquoise. Glass imitations of transparent gemstones usually are simple to identify. However, they are made to duplicate very closely the color and properties of some gemstones, with refractory angular materials added to the melt to simulate the flawed appearance of a natural gemstone. The fashioned stones are then mounted so that a prong prevents a refractometer reading. Such an imitation of emerald mounted in platinum with diamonds has fooled many a pawnbroker and many a jeweler.

Doublets made of two pieces of diamond or one of diamond and one of glass or zircon, and mounted to conceal the separation plane, are also

found. A colorless gemstone may be coated to impart a beautiful color and then mounted to protect the coated pavilion from detection. Magnification with proper lighting will detect such efforts to defraud.

One difficult identification for the gemologist is the separation of cultured from natural pearls. Since the surface layers of nacre deposited by the mollusk are essentially identical, only a study of the interior will permit identification. The most practical method of identification is x-radiography. The nucleus used in pearl culture is a bead fashioned from the shell of a fresh water pelecypod. Before accreting nacre, the host mollusk deposits a fairly thick layer of conchiolin, a substance considerably more transparent to x-rays than either the shell bead or the new nacre. As a result, the cultured pearl shows a heavy dark circular line on the negative a fraction of a millimeter from the outer edge.

A clue to identity is furnished by the fact that the fresh water shell used in pearl culture operations fluoresces strongly under x-rays, while the salt water pearls do not. Using soft x-rays and an immersion technique to counteract the spherical shape of the pearls, x-radiography provides an exact means of identification.

For the most part, gem materials may be identified conclusively by refractometer, polariscope and binocular microscope. Sometimes a specific gravity determination is an additional requirement. The dichroscope often is useful. Even particularly difficult identifications of transparent faceted material very rarely require any additional tests. That historical gemtesting device, the hardness point, is almost never employed by the trained gem man. Instruments designed specifically for his needs and fairly recent improvements of his testing techniques have enabled the trained gemologist to identify gem material with assurance and dispatch.

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NOTES AND NEWS

LABORATORY DEMONSTRATION OF THE NATURE OF INTERFERENCE COLORS PRODUCED BY A QUARTZ WEDGE BETWEEN POLAROID^s*

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In the laboratory the nature of the interference colors produced by the quartz wedge between polaroids may be easily demonstrated. The value of the demonstration has been established by repeated use in teaching elementary crystal optics.

An ordinary quartz wedge, such as is used with a polarizing microscope, is mounted over a slit which is parallel to the length of the wedge.

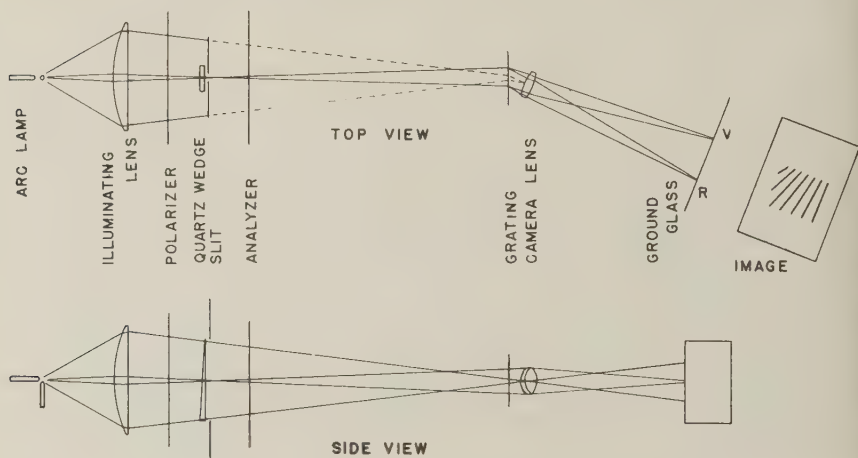


FIG. 1. Schematic demonstration of the spectral composition of quartz wedge interference colors.

The slit is of the same length as the wedge, and may be about 1 mm. wide. The wedge is placed between a pair of polaroids, at least one of which is arranged to rotate in the usual manner. The vibration direction of the polarizer is set at 45° to the vibration directions of the wedge. An arc lamp is placed behind the slit, wedge, and polarizer, and a lens, whose diameter is slightly greater than the length of the slit, is placed close to the slit on the side of the arc lamp. The arc is placed conjugate to the lens of a long bellows extension plate camera. This method of illumination produces a very even and fairly intense illumination of the slit and quartz wedge. The camera is mounted so that an image of the slit may

* Contribution from the Department of Mineralogy and Petrography, University of Michigan, No. 192.

be focused on the ground glass of the camera. A transmission replica grating, crossed with respect to the quartz wedge, is placed before the camera lens. The camera is fixed so that a first order spectrum is focused on the ground glass. The above arrangement is satisfactory for demonstration to small groups of students. The arrangement of apparatus is shown in Fig. 1.

The interference pattern exhibited by the wedge between crossed (Fig. 2) and parallel (Fig. 3) polaroids is readily appreciated by the beginning student. For crossed polaroids the dark bands represent a retardation of $n\lambda$ and each light band represents a retardation of $(2n+1)/2\lambda$. Of course, for parallel polaroids the reverse is true.

Since the retardation introduced by the crystal plate is proportional to the thickness of the plate, and the wedge has a uniform taper, the retardation scale parallel to the slit is linear. As quartz possesses very little dispersion of birefringence, the retardation scale is valid, for all ordinary purposes, for all wavelengths. The grating used as indicated above gives a practically linear dispersion at right angles to the slit. Consequently, the light and dark bands are portions of straight lines passing through the origin, if the small dispersion of birefringence is neglected.

The spectral nature of any interference color within the limits of the wedge can be seen at a glance. Upon rotation of one of the polaroids from the crossed position, the intensities of the light and dark bands change until at 45° an evenly lighted spectrum is seen, since only one of the vibration components transmitted by the quartz reaches the analyzer. As this 45° position is passed, dark bands reappear in the position previously occupied by the light bands.

An informative exercise for the student is the graphical construction of a retardation scale on a print similar to that shown in Fig. 2. The actual photograph is made with an ordinary desk type fluorescent lamp placed behind the polarizer, without the illuminating lens. When the photographs are taken in this manner, an essentially continuous spectrum, punctuated by the strong mercury lines, is produced. The mercury lines provide wavelength markers in the spectrum. The construction is most easily carried out by interpolating on the linear wave length scale to $500\text{ m}\mu$ and drawing a vertical line on the print corresponding to this wave length. Then the intersection of the dark bands with this line are projected horizontally to the retardation scale. Thus the retardation scale is marked in convenient $500\text{ m}\mu$ units.

The slight displacements of the bright spectral lines where the latter cross the dark interference bands are due to the use of an unusually long slit and the absence of a collimating lens before the grating. Their presence, which could be avoided by the use of a suitable collimator, does not detract appreciably from the value of the exercise.

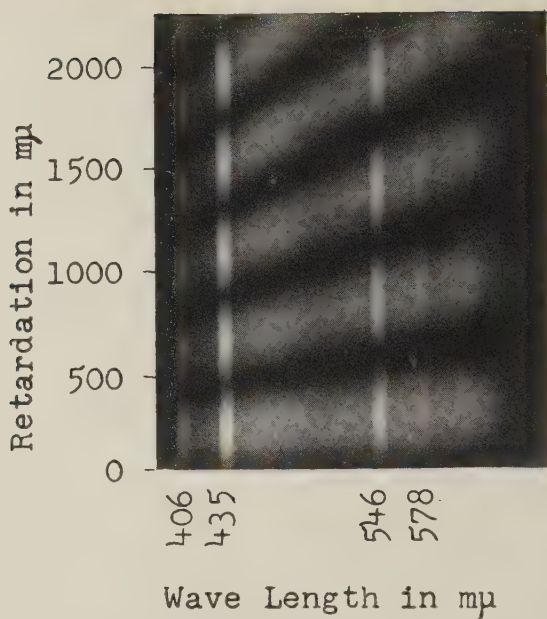


FIG. 2. Dispersed image of quartz wedge between crossed polaroids.

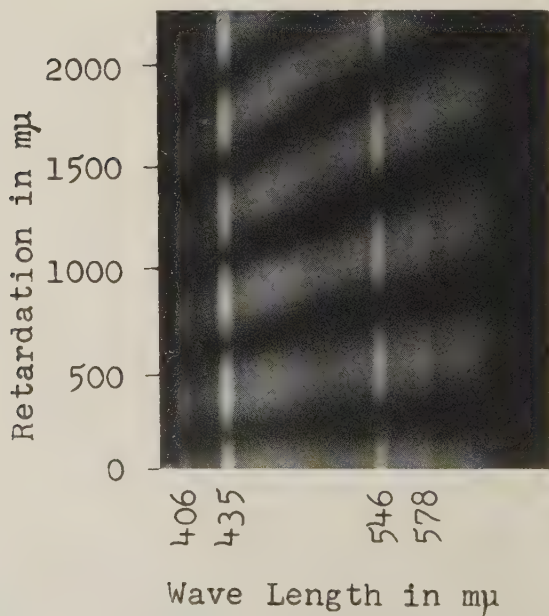


FIG. 3. Dispersed image of quartz wedge between parallel polaroids.

Incidentally the principle of calibrating retardation devices with the aid of a spectrometer is also illustrated.

An instructive variation of the experiment is to arrange both polaroids to rotate synchronously, which demonstrates that, as a crystal is brought from a position of maximum illumination to extinction, the amplitudes of the light waves passed by the analyzer vary, but the phase relations remain unchanged.

An interesting modification for advanced students of crystal optics would be to substitute for the quartz wedge a wedge of a substance showing strongly "anomalous" interference colors. If a substance exhibiting considerable dispersion of birefringence were substituted for the quartz, the interference bands would not be segments of straight lines passing through the extrapolated zero wavelength. In this case the retardation scale would be different for each wavelength. Even in the case of the quartz wedge the bands do not intersect at the origin; actually they intersect on the positive side of the wavelength zero. The displacement is of the order of $50\text{ m}\mu$ which is in agreement, within the large experimental error, with published data on the indices of quartz.¹

Photographs essentially similar to Figs. 2 and 3 were published by Hauswaldt.²

¹ Handbook of Chemistry and Physics, edited by Charles D. Hodgman and Harry N. Holmes, Chemical Rubber Publishing Company, Cleveland, Ohio, 1941, p. 2103.

² Hauswaldt, Hans, *Interferenzerscheinung im Polarisirten Licht*, Neue Folge, 1904, Plates 26, 27, 28.

THE PRIMITIVE CELL OF JOHANNITE

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The pseudo-monoclinic cell of johannite $\text{Cu}(\text{UO}_2)_2(\text{SO}_4)_2(\text{OH})_2 \cdot 6\text{H}_2\text{O}$ (Peacock, 1935), with morphological axial elements

$$a:b:c=0.9182:1:0.3799, \\ \alpha=90^\circ 54\frac{1}{2}', \quad \beta=90^\circ 38', \quad \gamma=110^\circ 37',$$

is all-face-centered (F). The cell obtained from it by transformation $\frac{1}{2}0\frac{1}{2}/0\frac{1}{2}\frac{1}{2}/001$ (Hurlbut, 1950; quoted by Palache, Berman, and Frondel, 1951) is primitive (P) but unconventional in that it is referred to a left-handed system of coordinates.¹

The conventional P cell is obtained from the F cell by transformation $\frac{1}{2}0\frac{1}{2}/0\frac{1}{2}\frac{1}{2}/001$. The axial elements, calculated from Peacock's numerical values, are

¹ The figure given by Hurlbut (1950, p. 533) should be relabelled as follows. Instead of c_0 read $-c_0$ and instead of c_0' read $-c_0'$. For each cell the origin is to be taken at the lattice node where the three labelled edges meet.

$$a:b:c=0.9305:1:0.7140,$$

$$\alpha=110^{\circ}\frac{1}{2}', \beta=111^{\circ}59', \gamma=100^{\circ}18''$$

The lengths of the primitive translations follow from Hurlbut's c value. They are:

$$a=8.90 \text{ kX}, \quad b=9.57 \text{ kX}, \quad c=6.83 \text{ kX}, \quad \text{with } V=474.4=1897/4 \text{ kX}^3;$$

or

$$a=8.92 \text{ \AA}, \quad b=9.59 \text{ \AA}, \quad c=6.84 \text{ \AA}, \quad \text{with } V=477.1=1908/4 \text{ \AA}^3.$$

This cell is the Delaunay reduced cell (with all three angles obtuse, Delaunay, 1933; Donnay and Nowacki, 1954, pp. 139–141). It happens to be defined by the shortest three translations of the lattice (its a length is shorter than Hurlbut's a_0').

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STUDIES IN THE MICA GROUP; MANGAN-MUSCOVITE FROM MATTKÄRR, FINLAND

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In a series of recent papers Heinrich and Levinson (1955*A*, 1955*B*) and Levinson (1955) have reported a significant frequency of polymorphism among muscovite-type (heptaphyllite) micas. It has been noted, moreover, that these micas exhibit considerable isomorphous substitution when compared with the ideal or theoretical muscovite composition. Significant contents of V_2O_3 , BaO, SiO_2 or H_2O characterize the muscovite-type micas that have crystallized as the 1-layer monoclinic ($1M$) or 3-layer trigonal ($3T$) polymorphs, although some of these, particularly the high SiO_2 and H_2O varieties, also have crystallized with the common 2-layer monoclinic ($2M$) structure. Previously it had been generally accepted, on the basis of the work of Hendricks and Jefferson (1939), that muscovite occurs only as the $2M$ polymorph. Axelrod and Grimaldi (1949), however, described a muscovite from Sultan Basin,

* Contribution from the Department of Mineralogy and Petrography, University of Michigan, No. 193.

Washington, which is now known to have a $3T$ structure (Levinson, 1955). This is the only reported mica with a composition close to the theoretical muscovite known to have a structure other than $2M$. The purpose of this note is to report the results of chemical and x -ray studies on an unusual mangan-muscovite (Eskola, 1914) which exhibits very little isomorphous deviation from the theoretical muscovite composition but has crystallized as the 1-layer monoclinic ($1M$) polymorph rather than the common or "normal" $2M$ form.

Eskola (1914, p. 37), in describing the pegmatites of southwestern Finland, briefly notes:

"A particular manganese-mineral, an intensely blue-coloured, fine-crystalline manganese-muscovite, containing 2.30% MnO, was found at Mattkärr."

This or similar material was studied spectrochemically by Erämetsä, Sahama and Kanula (1943), who determined the presence of 1% Rb_2O and 0.03% Cs_2O . Pehrman (1945) also describes a blue "radial" mica from Mattkärr, that probably represents similar material. He found it to have $2V = 39^\circ 20'$ by means of the universal stage.

A specimen of Eskola's mineral was borrowed from the Harvard Mineralogical Museum (No. 87441) for study. The material is deep purplish-blue (the color of some dumortierites), very fine-grained, and shows no megascopic structural features. Microscopic examination shows the mangan-muscovite to be colorless to pale lilac or pale purple in thin flakes. The flakes are actually aggregates of many very fine-grained mica shreds. The mangan-muscovite is mixed with an estimated six per cent of quartz as well as a few scattered grains of a mineral characterized by low birefringence, numerous minute inclusions, and $n = ca. 1.63$; it may be apatite.

X -ray powder patterns obtained from the mangan-muscovite confirmed the presence of a small amount of quartz. When quartz lines are subtracted the spacings and intensities characteristic of the 1-layer monoclinic ($1M$) mica polymorph remain. The x -ray data are recorded in Table 1.

The results of a quantitative spectrochemical analysis are presented in Table 2. The sum of the constituents determined in the analysis is 94.1 per cent; H_2O was not determined but undoubtedly accounts for the remainder. The following elements were not detected: Rb, Cs, Li, Sn, Ti, Co, Sc, Cr, V and F. In view of the fact that approximately six per cent of the bulk material consists of quartz the analysis is recast with this impurity deducted (Table 2). The recalculated results show a SiO_2 content of 45.7 per cent, which is in good agreement for a muscovite of normal composition. The MnO content of 1.7 per cent is high for a muscovite, however. The CaO content of 1.12 per cent possibly may be attrib-

TABLE 1. X-RAY POWDER DATA FOR MANGAN-MUSCOVITE
(Filtered copper radiation; $\lambda\text{CuK}_{\alpha 1} = 1.54050 \text{ \AA}$)

$d(\text{\AA})$	I	$d(\text{\AA})$	I
10.0	S	2.38	M
4.98	M	2.25	W diffuse
4.49	M	2.14	MW
4.38	VW	2.00	MS
4.11	VW	1.96	VW
3.65	M	1.72	VW
3.33	S	1.65	M diffuse
3.07	M	1.50	M
2.80	W	1.43	VWV
2.69	W	1.35	MW
2.57	MS	1.30	MW
2.46	W	1.25	W

uted in part to apatite, but inasmuch as the occurrence of this mineral within the mangan-muscovite is still in doubt, apatite has not been considered in the recalculation.

It is concluded that the composition of the mangan-muscovite from Mattkärr is close to that of ordinary muscovite and that it is the first mica with such a composition to be reported as having the *1M* structure. It seems doubtful that the *1M* crystallization can have resulted from the presence of 1.7 per cent MnO , because Whitmore, Berry and Hawley (1946) have found that the *2M* muscovite polymorph can accommodate as much as 4.81 per cent Cr_2O_3 . Undoubtedly both Cr and Mn occupy octahedral positions, isomorphously replacing Al, in the mica structure,

TABLE 2. CHEMICAL DATA ON MANGAN-MUSCOVITE

Constituent	Experimental	Corrected*
SiO_2	49	45.7
Al_2O_3	32	34.0
K_2O	10	10.6
Fe_2O_3	0.15	0.16
MgO	0.21	0.22
Na_2O	0.08	0.085
MnO	1.6	1.7
BaO	0.0008	0.0008
Ga_2O_3	0.012	0.013
SrO	0.004	0.004
CaO	1.05	1.12

Spectrochemical analysis by C. E. Harvey.

* Recalculated to eliminate quartz contamination estimated to be 6 per cent.

and Cr^{+3} and Mn^{+3} have nearly the same ionic radii. The effect of environmental factors cannot be evaluated owing to the lack of paragenetic data, but from the fine grain size and a comparison with the formation of other pegmatitic manganiferous muscovites, the mineral probably is hydrothermal rather than magmatic in origin.

On the basis of the low Fe_2O_3 content (.16 per cent) in relation to the 1.7 per cent MnO , the intense purplish-blue color can be related to the Mn chromophore (Heinrich and Levinson 1953). Very likely the intensity of the color in hand specimen is in part a function of the very fine grain.

This work was supported in part by the U. S. Army Signal Corps Squier Signal Laboratory as Project M978 of the University of Michigan Engineering Research Institute. We are thankful to Dr. S. Benedict Levin, administrator of the project, for his continuous support and to Professor Duncan McConnell for critically reading the manuscript.

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STRESS AND DOUBLE REFRACTION IN DIAMOND*

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It has become accepted as axiomatic that anomalous double refraction in diamond is due to intense internal strain that makes crystals showing high interference colors unsatisfactory for some industrial uses. This is especially true for wire drawing dies and shaped diamond cutting tools which are made from the finer grades of industrial diamonds. In practice the examination of crystals between crossed polars has never been deemed necessary for some of the less specialized uses of industrial diamonds such as wheel trueing and core drilling, but in some companies it is standard practice to examine all diamonds with a polarizing microscope before cutting for industrial use.

* Contribution from the Department of Mineralogy and Petrography, University of Michigan, No. 194.

In 1952-53 several thousand industrial stones of the type known as "flats" were examined in this laboratory under an Office of Naval Research grant to select for study outstanding specimens showing either double refraction or inclusions. A few showing first and second order interference colors were found. When a carat nearly perfect octahedron was examined under the polarizing microscope while being compressed by a screw clamp, it was found that interference colors of the fourth or fifth order were easily induced. This interference color is far higher than that seen in diamonds not subjected to external mechanical stress and was induced by pressures so far below those to which industrial diamonds are subjected during use that it appears that no conclusions should be drawn from "anomalous" double refraction as to the suitability of any diamond for industrial use.

While the theoretical treatment of photoelasticity in diamond has been given (Pockels,¹ Coker and Filon,² Bhagavantam³) and the photoelastic constants have been determined by Ramachandran,⁴ it seemed desirable from a practical point of view to obtain directly information on the order of interference colors exhibited by an uncut octahedron of diamond under external stresses of known magnitude. To this end a single octahedral crystal was examined in polarized light under a series of compressional loads.

Force was applied normal to a pair of octahedral faces by means of thin edges of mild steel. If the indices (111) and $(\bar{1}\bar{1}\bar{1})$ are assigned to the faces being compressed, then the steel edges in contact with these faces were oriented with their lengths parallel to $[1\bar{2}1]$. The interference phenomena were observed by viewing the crystal in this direction (neglecting refraction) through faces $(\bar{1}\bar{1}\bar{1})$ and (111) . In other words pressure is exerted normal to opposite octahedral faces by V-wedges whose parallel edges bisect the 60° angles of each of the opposite octahedral faces. The crystal is viewed nearly parallel to the edges of the wedges. The distance between (111) and $(\bar{1}\bar{1}\bar{1})$ is 4.5 mm. The upper and lower contact areas are about 5.4 by 1.3 mm.

Figure 1a is a photograph of the diamond between the steel edges. The clips which hold the diamond in place can be seen on either side.

A series of photographs was taken of the diamond between opposed circular polars. Sodium light was used. The force exerted upon the diamond was 0, 50, 100, 150, and 200 kilograms. Figure 1b through f,

¹ Pockels, F., *Lehrbuch der Kristalloptik* (1906).

² Coker, E. G., and Filon, L. N. G., *Photoelasticity* (1931).

³ Bhagavantam, S., Photo-elastic effect in crystals: *Proc. of the Indian Academy of Sciences*, Section A, **XVI**, No. 6, 359-365. Dec. 1942.

⁴ Ramachandran, G. N., Photoelastic constants of diamond: *Proc. of the Indian Academy of Sciences*, Sec. A, **XXV**, No. 2, 208-219. February 1947.

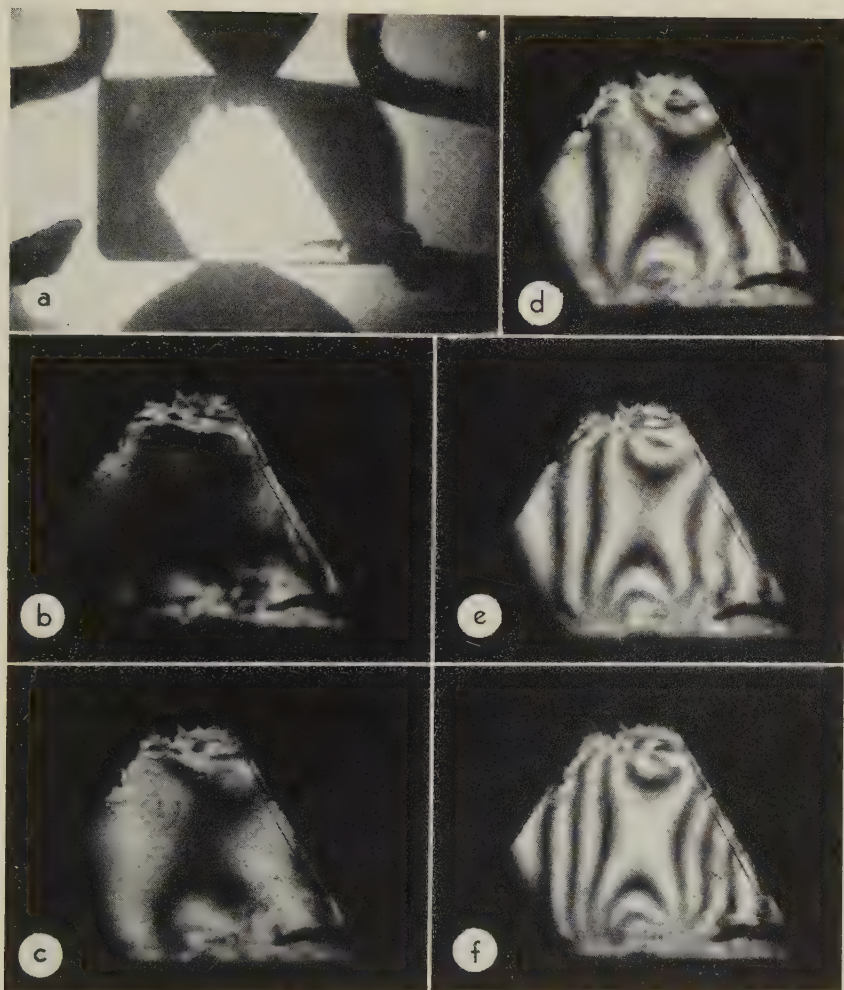


FIG. 1. (a) Diamond mounted in stress apparatus as viewed in the camera (reversed image). (b-f) diamond between opposed circular polars, sodium light, vertical compression. (b) 0 kilograms; (c) 50 kilograms; (d) 100 kilograms; (e) 150 kilograms; (f) 200 kilograms.

respectively, illustrate the interference patterns produced. It should be noted that since the diamond was immersed in an index liquid of 1.65, only light passing through plane $(1\bar{1}1)$ was recorded. The photographs yield information on the magnitude of the difference between compressional and tensional stress normal to the line of sight. The equal path difference curves do not yield information of the direction of these stresses. One striking feature of the pattern is that the distribution of the equal path difference curves does not substantially differ in appearance from what one would expect from a mechanically isotropic (amor-

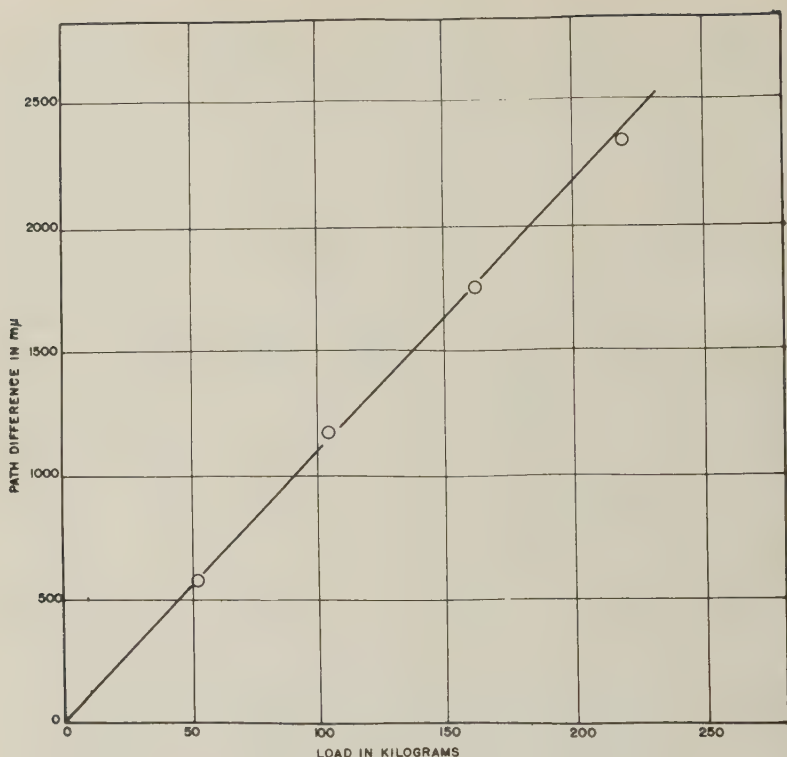


FIG. 2. Path difference plotted against compression in kilograms.

phous) substance. This was checked with a glass model under similar conditions. The fast vibration direction lies in the direction of compression.

The relation of the path difference at the center of the field to the total load applied is indicated in Fig. 2. If it is assumed that the stress is uniformly distributed along the line of sight, then the birefringence of the diamond can be readily obtained for any selected portion of the field and at any load.

Since externally unstressed diamonds of size similar to the crystal under study do not show interference colors as high as third order, it can be seen that examination in polarized light to eliminate stones in a high state of strain is probably unwarranted. It must, however, be remembered that the observed interference color of natural internally stressed stones is determined by the total retardation of a given thickness of the crystal. It may be that most of the stressed portion which produces the retardation lies within a thin element of the crystal. If this is true, the birefringence—and hence local stress—could be considerably greater

than that encountered in the experiments here described. Whether the birefringence of natural (not externally stressed) stones is due to stress is perhaps debatable.

A BERTRAND-LASAULX SLIDER FOR THE POLARIZING MICROSCOPE

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Almost fifty years ago Wright suggested the use of a pair of right-angled prisms in an insertable metal plate to permit observation of an interference figure by the Lasaulx method without the trouble of removing the ocular and replacing it with a pinhole eyepiece. Six years later he proposed that a single rhomboid prism be employed in place of the earlier pair. This apparatus seems not to have been adopted by the microscope makers.

At the time Wright made his suggestion, it was not very common to use the polarizing microscope for determining the indices of refraction of a mineral grain by means of comparison with an embedding liquid. Although this technique has become well-nigh universal since World War 1, and while microscopists recognize the great value of the Lasaulx method when working with crushed grains (or indeed with *small* grains in a thin-section), the reflecting apparatus has not gone into production.

Some years ago the writer approached microscope manufacturers with the suggestion of making a double slider—Bertrand lens one way, Wright-Lasaulx prism the other. This was finally done by the American Optical Company through the good influence of the late Joseph D. Reardon. As first made the new slider replaced the standard Bertrand one and a small auxiliary pinhole tube was clamped along the side of the microscope tube. The latter, while made at my suggestion, turned out to be relatively cumbersome; it also was not easy to have it properly centered over the prism. Accordingly I had our shop replace it with a small pinhole tube attached directly to the slider as shown in the photograph. While this pinhole tube lacks an elegant appearance, it does not get in the way and can be covered easily by a shell vial if one feels that a dust cap is needed. It can be centered once for all by having the pinhole cover held to the top of the tube (or the base of the tube fastened to the slider) by means of three screws going through enlarged holes. If one wishes to use a camera lucida the slider is very quickly removed from the microscope tube; or the slider might be mounted with the Bertrand on its right side, the pinhole tube on the left. Experience indicates that a pinhole 0.04 inches in diameter gives optimum results; this is smaller than the one usually supplied by the manufacturer.

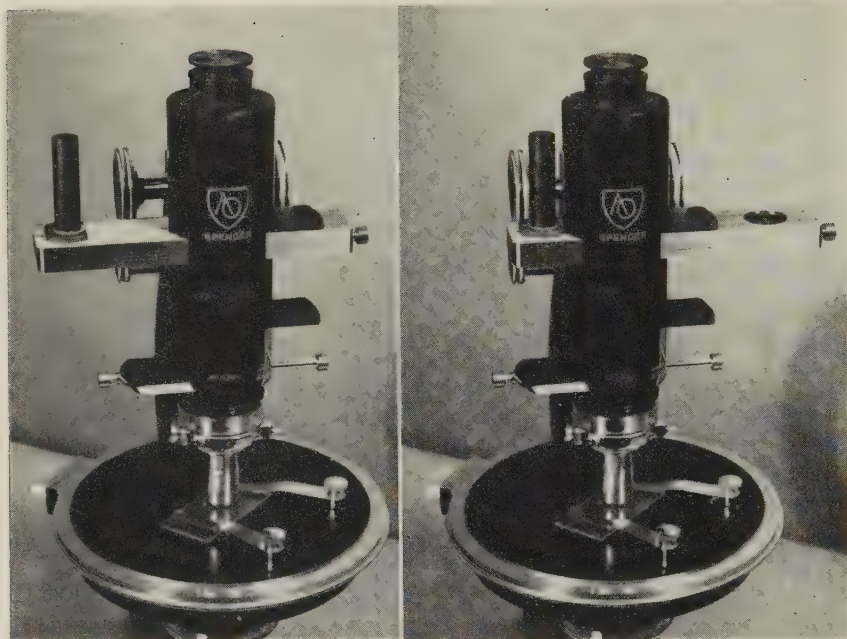


FIG. 1. Polarizing microscope with the Bertrand-Lasaulx slider. *Left*, the slider is in position for ordinary orthoscopic examination. *Right*, the slider is pushed to the Lasaulx conoscopic position; the eye now looks down the small pinhole tube.

Workers who have used the new slider find it highly satisfactory. The sharper and more brilliant isochromes make errors of interpretation much less likely than is true when using the Bertrand; the latter is still valuable where measurements are needed, unless one has a reticle in the objective with a micrometer scale (Lenk) or concentric rings, or an objective Iris diaphragm (Slawson).

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MONTEBRASITE FROM EIGHT MILE PARK,
FREMONT COUNTY, COLORADO*

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In 1911 Schaller described a member of the amblygonite group from a pegmatite on Eight Mile Park, west of Canon City, Fremont County, Colorado (Schaller, 1911, 1912), proposing for it the name natramblygonite, which he later withdrew because of etymological objections, and substituted for it fremontite (Schaller, 1914, 1916). In the amblygonite group, $(\text{Li}, \text{Na})\text{AlPO}_4 (\text{F}, \text{OH})$, the now generally accepted nomenclature is:

	<i>Li > Na</i>	<i>Na > Li</i>
<i>F > OH</i>	amblygonite	(not known)
<i>OH > F</i>	montebrasite	natromontebrasite

Thus fremontite (Table 1, Anal. A), in which $\text{Na}:\text{Li}=1.7:1$ and $\text{OH} > \text{F}$, becomes natromontebrasite and possesses the dubious distinction

TABLE 1

	<i>A</i>	<i>B</i>
Li_2O	3.21	5.02
Na_2O	11.23	6.23
Al_2O_3	33.59	35.77
P_2O_5	44.35	45.87
F	5.63	tr.
H_2O	4.78	7.04
K_2O	0.14	n.d.
	102.93	
O = F	2.37	
	100.56	99.93

A. Natromontebrasite, Meyers Quarry pegmatite, Eight Mile Park, Fremont Co., Colo. Analyst—W. T. Schaller (1911).

B. Montebrasite, Meyers Quarry pegmatite, Eight Mile Park, Fremont Co., Colo. Analyst—Alice S. Corey.

of having been referred to under three different names within 40 years. The occurrence on Eight Mile Park is the only one known, and it was found there only in one place in the Meyers Quarry pegmatite.

A few fragments of natromontebrasite were collected by the senior

* Contribution No. 195 from the Department of Mineralogy, University of Michigan.

author in the summer of 1946, and its paragenesis has been described (Heinrich, 1948). In June 1951 the senior author discovered several specimens of an amblygonite-group mineral in a new opening in the Meyers Quarry pegmatite, and in the summers of 1952 and 1953 much more material was uncovered. The identity of the mineral was checked by means of an x -ray powder photograph.

The new cut was made in the south side of the Meyers Quarry pegmatite near its western end along a small gulch 200 feet southeast of the original fremontite locality, as shown on the map of the western part of the pegmatite (Fig. 22, p. 582, Heinrich, 1948). The amblygonite mineral and its associates were exposed on bench of the cut along its eastern wall.

The pegmatite in the cut, like much of the Meyers Quarry deposit, is indistinctly zoned. Remnants of small core pods of large microcline crystals are exposed, but most of the pegmatite consists of a granitic to subgraphic, variably grained, quartz-microcline aggregate, together with small quartz pods, microcline blocks, muscovite books and masses of intergrown quartz-muscovite.

The cleavelandite-red muscovite pegmatite, in which the montebrasite occurs, is restricted to the margins of one of the microcline core pods, forming an irregularly bounded unit whose contacts transgress the fabric of the microcline-quartz rock. The cleavelandite pegmatite includes corroded and veined relicts of microcline crystals as much as six inches long.

The main minerals in the cleavelandite rock are (in approximate order of abundance): cleavelandite, fine-grained bronze to red muscovite, quartz, microcline, tourmaline, green muscovite in large books, beryl, monebrasite, spessartite and apatite. The rock originally consisted chiefly of microcline and quartz with subordinate crystals of spessartite, books of greenish muscovite, masses and rude crystals of montebrasite, blocks and crystals of yellow beryl, tourmaline crystals, and a few crystals of apatite. All of these show replacement, corrosion and veining by cleavelandite and the fine-grained bronze muscovite, which itself replaces cleavelandite.

Montebrasite occurs mainly as chalky white, rounded, single-crystal masses with scallopy margins, averaging about $1\frac{1}{2}$ inches in length, although some pieces and a few rudely faced crystals as much as six inches long appear. Forms noted are a (100), b (010) and c (001) (Fig. 1). The mineral is markedly twinned both megascopically (Fig. 1) and microscopically (Fig. 2), into two individuals of about the same size and in some pieces polysynthetically as well (Fig. 2).

Most of the rounded pieces occur in reddish brown cleavelandite and are separated from the feldspar by a thin but conspicuous, fine-grained,

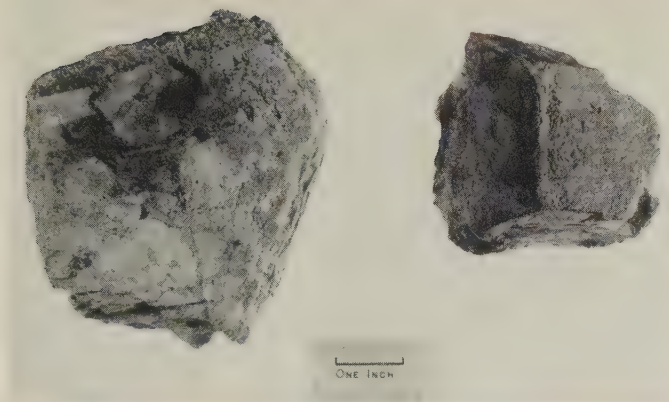


FIG. 1. Rude crystals of montebrasite, Meyers Quarry pegmatite, Eight Mile Park, Colorado. Crystal at left twinned.

dark brown shell. Under the microscope the shell (Fig. 3) is seen to consist usually of two parts—an outer zone of fine-grained muscovite stained by hematite and an inner unit of brown cryptocrystalline material that has very low birefringence and a general index of refraction considerably

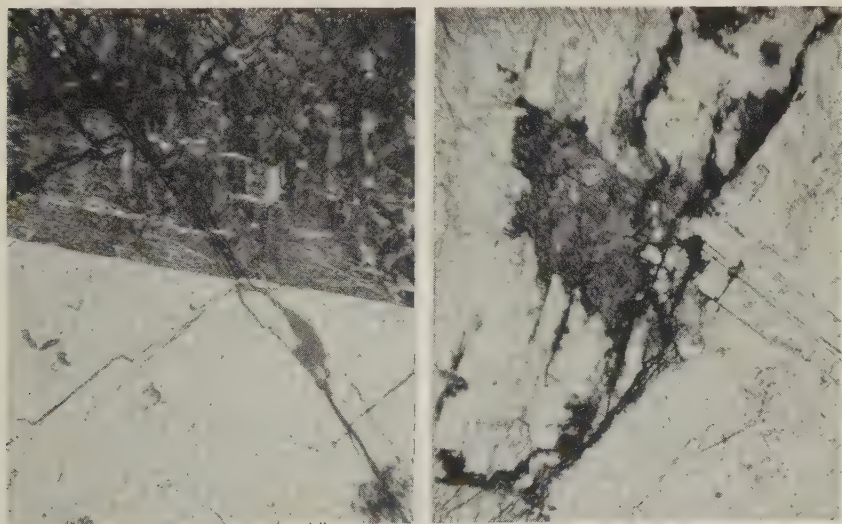


FIG. 2 (left). Photomicrograph of twinned montebrasite from Eight Mile Park, Colorado. Nicols crossed, $\times 22$.

FIG. 3 (right). Fine-grained, dark brown alteration of montebrasite, Eight Mile Park, Colorado. Nicols not crossed, $\times 22$.

below both the montebrasite and muscovite. This material apparently has formed as a byproduct in the replacement of the phosphate by muscovite or by cleavelandite, for it corrodes the montebrasite marginally and extends into it in veinlets along and across twin boundaries and cleavages. Attempts to identify the fine-grained material by *x*-rays proved unfeasible owing to extensive contamination by iron oxide. However, the alteration is apparently similar to that described by Quensel (1937) for amblygonite from Varuträsk, Sweden, and from its optical properties the fine-grained mineral may well be a clay.

The sequence of mineral formation is:

- A. Magmatic
 - 1. Microcline, spessartite, apatite, quartz
 - 2. Green muscovite, beryl
 - 3. Black tourmaline
- B. Hydrothermal
 - 4. Blue tourmaline
 - 5. Green tourmaline
 - 6. Red tourmaline
 - 7. Montebrasite
 - 8. Cleavelandite, quartz, bertrandite (?)
 - 9. Bronze muscovite, clay mineral
 - 10. Hematite
- C. Minor fracturing
- D. Supergene
 - 11. Local leaching
 - 12. Calcite crusts in vugs

The composition of the original natromontebrasite (*A*) is compared with that of the newly-discovered amblygonite mineral (*B*) in Table 1. Although the analysis of the new material has a slight deficiency of alkalis and a slight excess of H₂O over that required by the theoretical composition (the latter is not uncommon in amblygonite analyses), the two minerals differ considerably in their Na-Li and OH-F ratios. In the newer material the Na:Li ratio is 1:1.7 and this mineral is thus montebrasite and is not identical with the natromontebrasite of the original find.

As early as 1893, Des Cloiseaux (1893) pointed out that two distinct members of the amblygonite family occurred at the same locality, Montebras in Soumans, Central Plateau, France. Others who have demonstrated the presence of more than one type or generation of amblygonite in a single pegmatite or in related pegmatites include Landes (1925) in the Buckfield, Maine, pegmatites; Quensel (1937) in the Varuträsk pegmatite, Sweden; Palache et al. (1943) in the Newry, Maine, pegmatite and Dana (1873) and Palache et al. (1943) in the Hebron, Maine, pegmatite.

Thus it appears that occurrence of two or even more generations (Varuträsk has three) of amblygonite with distinct compositional differences may not be rare in single pegmatites or related pegmatites. The data are as yet insufficient to indicate any systematic relationship between composition and paragenetic position (Heinrich, 1953).

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INTERNATIONAL UNION OF CRYSTALLOGRAPHY

The International Union of Crystallography in collaboration with Consejo Superior de Investigaciones Científicas will hold a symposium on "Structure on a scale between the atomic and microscopic dimensions" in Madrid, Spain, April 2 to 7, 1956. The results obtained by various well-known and new techniques including *x*-ray and electron diffraction and microscopy will be discussed. Those wishing to present papers should send the title and a 10 line abstract to the program chairman prior to January 1, 1956: Prof. A. Guinier, Conservatoire National des Arts et Metiers, 292 Rue St. Martin, Paris (3e), France. Two I.U.Cr. Commissions (Crystallographic Apparatus and Crystallographic Teaching) will also hold meetings during this period. Further information may be obtained from the secretary of the local committee: Dr. M. Abbad, Serrano 118, Madrid, Spain.

The Fourth General Assembly and International Congress of I.U.Cr. will be held at McGill University, Montreal, Canada, July 10-17, 1957, and will be followed by two Symposia July 18-19. Additional information will appear as notices in *Acta Crystallographica*.

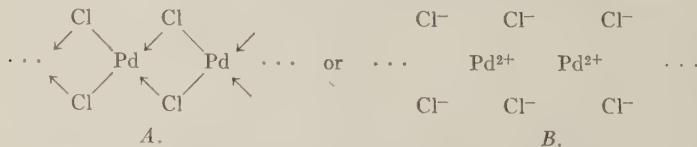
BOOK REVIEWS

FRITZ EPHRAIM'S INORGANIC CHEMISTRY

SIXTH ENGLISH EDITION. By P. C. L. THORNE AND E. R. ROBERTS. Oliver and Boyd Ltd., Edinburgh and London. Interscience Publishers Inc., New York, N. Y. Pp. xii and 956. Figs. 96; 1954. Price \$6.25.

According to the announcement of this new edition, the sections on Valence and on Radioactivity have been largely rewritten. The review of the fourth edition in the *American Mineralogist*, **32**, 97 (1947) emphasized the difficulties in presenting the electronic structure of molecules and crystals caused by the existence of widely divergent approaches to this aspect of "Valency." It is therefore rather satisfying to find that in the present edition these different points of view are explained more thoroughly than before and are applied throughout the book. In particular two theories are compared systematically in the case of relatively simple compounds. One is closely related to the scheme of classical valence bonds, interpreted by shared electron pairs. The difficulties of this approach, especially in the case of inorganic substances, have grown over the decades and some authors attempt to overcome them by applying the picture of multiple "structures contributing" to an experimentally unique molecular species. The other theory emphasizes the electrical attractive and repulsive forces acting between the atomic nuclei or cores and quantized groups of electrons. It succeeds in representing even the most complex compounds by single formulas. The difficulties which arose in the application of these two theories to SO_4^{2-} and SiO_4^{4-} in the fourth edition have been removed now on pp. 601 and 857. Discussing the structure of chlorine-oxygen compounds (pp. 382-4) the authors state: "The relative merits of these two views are left for the reader to assess."

Characteristic of this book since its first appearance in 1922 is the considerable space devoted to coordination compounds. The term coordination number, so important now also in considerations of crystal structure, was introduced by A. Werner in 1893. It was intended to express the fact that in many compounds an atom can be connected with a larger number of other atoms than its usual valency would allow. Hence, Werner distinguished main and secondary valences and represented the first ones in the customary way by solid lines, the others by dotted lines. This distinction is preserved in scores of formulas to be found in the present book as well as in an overwhelming part of recent literature. The main modernization consists in drawing, instead of a dotted line, an arrow which expresses the assumption that in such a secondary or coordinative bond the shared electron pair originated in one atom only. As an example formula *A* may serve which together with formula *B* are given on p. 358 of the book as alternatives for representing the structure of the chains



in $(\text{PdCl}_2)_n$. However, the fact that the experimentally known structure of these chains in crystalline PdCl_2 shows only *one* internuclear distance (2.31 Å) between Pd and Cl, disproves the assumed distinction between true and coordinative covalent bonds.

Analogous contradictions were known to Werner and the first step for their resolution was made by W. Kossel in 1916. He took into account the electric nature of the binding forces and arrived e.g. at the conclusion that a cation A^{n+} , after having attached to itself n rigid anions B^{1-} exerts on a further B^{1-} an attraction which is stronger than the repulsion exerted by the n anions. These simple calculations do not explain why the coordination in

PdCl_2 is so different from that in MgCl_2 although $\text{Pd}^{2+}\text{F}^-_2$ and $\text{Mg}^{2+}\text{F}^-_2$ have both the rutile structure and differ little with respect to internuclear distances. The answer can be found in points of view developed since 1923, if one formulates PdCl_2 as is done in formula *B*: the polarizability of Cl^- is much larger than that of F^- and the polarizing power of Pd^{2+} , which has not the noble gas type of Mg^{2+} , is more pronounced than that of the latter. These factors are responsible for the strengthening of the binding between Pd^{2+} and Cl^- .

For all these reasons the undersigned considers formula *A* and its numerous analogues as anachronistic. It would be a considerable further improvement of this book, if in a later edition formulations which allow the reader to recognize the electric nature of the binding as does formula *B*, were applied to the majority of coordination compounds. It can be only mentioned here that the presentation of some other topics was also taken over from former editions and needs adjustment in view of new developments.

The additions to the chapter "Radioactivity and Isotopes," as compared with the fifth edition, involve the table containing the four radioactive series as well as nuclear fission and the transuranic elements.

The new edition will again fill its well deserved place among advanced treatments of an important branch of chemistry.

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University of Michigan, Ann Arbor, Michigan*

DIE MINERALFUNDE DER SCHWEIZER ALPEN, by ROBERT L. PARKER, Wepf and Co. Verlag, Basel, 1954. viii+311 pages, with 2 panoramas and a colored map showing mineral localities. Price Sw. Fr. 36.00 or D.M. 34.60 (ca. \$7.50).

This nicely printed and attractively illustrated book is essentially a second edition of Parker's earlier (1940) *MINERALVORKOMMEN*, which appeared as Part II of Volume I of *Die Mineralien der Schweizeralpen*, by P. Niggli, J. Koenigsberger, and R. L. Parker [*Am. Mineral.*, **28**, 58-60, 1943].

The treatise has been brought up-to-date and completely reworked. The text is almost twice as long as the original and the numbers of plates and figures are much more than doubled.

The book starts off with a 16 page description of 26 characteristics Alpine mineral assemblages. The main portion of the text (216 pages) is a catalogue of the occurrences of these assemblages in 13 regions of the Swiss Alps. There follows a 14 page determinative table for identifying the various species. The alphabetical list of species, with references to the text, occupies 28 pages; the literature references, 20; and the list of mineral localities, 10. References to localities are by pages and appear to be complete, but those for mineral species are much more general, page references being given only occasionally and lists of localities, especially for minerals that occur widely, being woefully incomplete.

There are no colored plates of minerals, but the photographs of minerals are well chosen and printed on excellent paper. It is a pleasure to see pictures of minerals that resemble the originals enough so that they can be recognized.

EARL INGERSON,
U. S. Geological Survey, Washington 25, D.C.

HOW TO KNOW THE MINERALS AND ROCKS, by RICHARD M. PEARL. McGraw-Hill Book Company, New York, 1955. 192 Pages, 8 colored plates. Price \$3.50.

Pearl's book is aimed at the amateur collector or prospector, or at the man in a touring car who would like to know what he sees on a trip whether he intends to collect it or not. Such a book can do a great service to its audience and to the science, but in order to do so effectively it should be even more nearly free from errors of fact and interpretation than a

book intended for the professional mineralogist or petrologist; the professional can check suspected inaccuracies for himself, but ordinarily the amateur does not have the means to do so and must take what he sees printed at face value.

It is very unfortunate, therefore, that there are so many errors in the book under review. The most noticeable inaccuracies are in the illustrations, both color photographs and the drawings. Very few of the colors in the plates are true and about half of them are completely off. The worst ones, which are apt to be actually misleading are:—

<i>Mineral</i>	<i>Color on plate</i>	<i>Color should be</i>
Chalcopyrite	Brown	Yellow
Franklinite	Blue	Black
Gold	Pinkish brown	Yellow
Selenite	Yellow	Clear or white
Hematite	Light blue	Dark red
Hematite	Green	Dark red
Limonite	Lavender	Yellow
Malachite	Light blue	Dark green
Pyrite	Green	Yellow
Jasper	Orange	Red
Rock crystal	Lavender	Clear
Rhodochrosite	Orange	Pink
Rhodonite	Orange	Pink
Variscite	Blue	Green

A few of the sketches of minerals are very good and should aid in identification, such as those of crystalline silver, galena, arsenopyrite, and stibnite. Most of the sketches of massive minerals, however, might better have been omitted, since they add nothing to the word picture given in the text. Some of them, such as those of covellite, graphite, gold, and tetrahedrite are likely to be misleading and hinder rather than help in identification. The sketches of rocks (pp. 165–186) are no better; except for those of porphyry, gneiss, conglomerate and obsidian they are likely to provide very little assistance in identifying rocks.

In the text there are many places where usage, interpretation, or classification is questionable, and there are also many outright errors in statements. Neither the minerals (pp. 56–160) nor the rocks (pp. 165–186) are arranged according to recognized classifications. In the general discussion of igneous rocks (pp. 19–21) it probably would have been better to substitute *diorite* for *monzonite* and to mention *rhyolite* as including *obsidian* and *pumice*. *Felsite* is a waste basket term for light colored aphanitic rocks and might better have been omitted in favor of more specific names like *trachyte* and *andesite*.

Volcanism (p. 20) properly includes only surface and near-surface manifestations of igneous activity; *vulcanism* is the term which “includes the behavior of all molten rock, whether it takes place on the surface or far below. . . .”

Many textural differences between extrusive rocks and chemically similar intrusive rocks are certainly due to differences in cooling rate. For the extreme example mentioned in the last paragraph of p. 20 (coarse pegmatite), however, there can be little doubt that the presence of abnormal quantities of water and other volatile constituents is more important than the cooling rate.

The statement (p. 22) that “Even the most deeply buried igneous rocks will someday be exposed by erosion” is open to serious question. There is good evidence that the igneous rocks beneath large parts of the ocean basins have never been exposed to erosion, and there are no cogent reasons for supposing that they ever will be.

On page 50 uraninite and pitchblende are said to be “cousins”: actually “twins” would be a more accurate relationship, since they are varieties of the same species. They are said

to be "the radioactive minerals described in this book," yet on page 92 it is said of carnotite "it is at present the only significant ore of uranium in the United States." Nor is this statement true; unoxidized ores of uranium have been in important production since long before Pearl's book went to press.

No authority is given for the statement (p. 94) that "deerhorns (are) found to have changed to cassiterite in the streams of Cornwall"; it is highly improbable that a substance as insoluble as in SnO_2 at ordinary temperatures and pressures could replace anything by the action of cold surface waters.

Other instances of questionable usage occur in the section on petrology. On page 161, for example, it is said that in hand specimens of rocks "there is scarcely any difference between texture and structure." Actually many, if not most, rocks (slate, phyllite, schist, gneiss, etc.) show structures that are visible in hand specimens, and are quite distinct from texture. On page 177 "expanded" would describe pumice better than "perforated"; also, fibers (l. 3) are rare in pumice, the shards that separate the open spaces being much more commonly segments of sphere-like surfaces.

The book is gratifyingly free from typographical errors. The locality listed as Lauvig, Norway, should be *Lawvik*.

As indicated above, there are many errors in statements throughout the book. For example, in the section on minerals "rhombic cleavage" is used both for orthorhombic prismatic cleavage (Fig. 25, p. 45) and for rhombohedral cleavage (rhombohedral carbonates, pp. 99-100, 114-115, and 117), but in two of the latter (rhodochrosite, p. 114, and siderite p. 115) the sketches show cleavages that look for all the world like orthorhombic pinacoidal!

The formulas given in the middle list on page 52 are for radicals, not compounds as stated. Gold is not "copper color" as indicated on page 62.

On page 106 kernite is said to occur only in the Mojave Desert of California, but it is now known to occur in considerable quantities in northern Argentina.

Sodalite is correctly characterized as having six cleavage directions (p. 108), but the illustrative sketch shows octahedra (4 directions) and cubes (3 directions).

The sketch showing the cleavage of pyroxene (p. 109) is also in error. Traces of two cleavages are shown approximately at right angles to each other, but they are not parallel to the unit prism, as they should be. The sketch of amphibole cleavages, on the other hand (p. 110), is correct.

Clear potassium feldspar (erroneously called "potash" feldspar by Pearl, p. 125) is by no means always orthoclase. Indeed, it is more apt to be sanidine or adularia.

It may be possible to induce quartz to scratch quartz (p. 151) under certain conditions where directions are favorable, but it certainly cannot be done readily enough for use as a key to identification.

Texture cannot always tell whether a rock is intrusive or extrusive (p. 161); the central part of a thick flow may be much coarser grained than the border facies of a fairly deep-seated intrusive.

Page 167, line 9, *iron* should read *iron oxide*.

The orbicules of orbicular granite are not composed of "foreign minerals" (bottom of p. 168), but are formed by an unusual concentration and arrangement of the normal minerals of the granite.

Smoky quartz is common in pegmatites, but this is by no means the only source, as stated on page 169. Smoky quartz occurs not only in non-pegmatitic granite, but also as large fine crystals in quartz veins with no trace of pegmatitic affiliations.

It is true that in areas of folded rocks the cleavage of slate is commonly developed at an angle to the original bedding (p. 180), but the two structures may also be parallel.

High pressure is not necessary for the formation of quartzite (p. 184); the cementation can be accomplished at elevated temperatures and relatively low pressure.

The "mineral content" of basalt is given as pyroxene and olivine (p. 186), whereas plagioclase feldspar (commonly labradorite), which is usually more abundant in basalt than pyroxene and olivine combined, is not mentioned in its description. The Deccan region of India (p. 186) is not a peninsula and contains nearer 200,000 square miles of basalt than half a million.

How to Know the Minerals and Rocks is interestingly written. Sections like "Soils and Scenery" (pp. 28-30) can create a desire in collectors to know more about the broader aspects of their hobbies. If another edition should be called for it is to be hoped that these sections could be expanded somewhat and the whole book re-written and edited much more carefully than was the current edition.

EARL INGERSON,
U. S. Geological Survey, Washington 25, D.C.

SOUTHERN AFRICA, A GEOGRAPHICAL STUDY: VOLUME II, ECONOMIC AND HUMAN GEOGRAPHY, by JOHN H. WELLINGTON. New York: Cambridge University Press, 1955. xviii+283 pages. Price \$6.50.

This is the second volume of a series dealing with all of Africa south of the Congo-Zambezi watershed, including the Union of South Africa, with South-West Africa, the High Commission territories of Basutoland, Bechuanaland and Swaziland, Southern Rhodesia (except the Northern Province), Nyasaland, Mozambique and Southern Angola. Volume I treated, in its three parts: Structure and Surface; Climate, Vegetation and Soils; and Hydrography.

The current volume is also divided into three parts: Land Utilization, 118 pages; Mineral and Other Industries, 82 pages; and The People, 69 pages. With so few pages devoted to so large an area treatment is necessarily brief, but the discussion of mineral resources is particularly sketchy, being limited to 48 pages. Of the 21 pages devoted to the gold deposits six are taken up with a discussion of the problem of water for the mines and two pages are devoted to labor problems. Diamonds and platinum together take up six pages and the tremendously important and interesting copper deposits are skimmed over in three pages. Coal is given eight pages; iron, six; asbestos, chromite, and manganese have one page each. None of the other varied mineral resources of the area are even mentioned.

The book can be recommended as a brief and general treatment of a large, important, and interesting area of the earth's surface, but not for any details of the geology or mineralogy of the region.

EARL INGERSON,
U. S. Geological Survey, Washington 25, D.C.

THE COLLOID CHEMISTRY OF SILICA AND SILICATES, by RALPH K. ILER. Cornell University Press, Ithaca, New York, 1955. xii+324 pages. Price \$5.50.

Into this little volume is compressed a great deal of information on properties and uses of colloids of silica and silicates. As would be expected from the author's connection (du Pont) emphasis is on applications to paint, oil purification, soil conditioning, paper and textile processing, latex products, commercial waxes, plastics, culture media, etc. Minerals are treated incidentally as raw materials, but much of the information in the book can have a bearing on problems of mineral genesis.

The section on clay minerals (pp. 190-217) is more complete and up-to-date than might be expected in a book of this kind. The nomenclature employed is that which is becoming accepted American usage. It is surprising to find that Iler uses the compositions and formulas of the clay minerals proposed by Ross and Hendricks (Minerals of the Montmorillonite Group, *U. S. Geol. Survey Prof. Paper* 205-B, 1945) without mentioning these authors or listing the publication in the bibliography. For the most part the references are very full and up-to-date.

Throughout the work "silicic acids" are discussed as if they were actual compounds that have been identified, although Iler recognizes (p. 127) that they "have not been isolated or characterized."

It is probably too late to stem the flood tide of usage, but the reviewer would like to make a belated plea for the use of the word "presently" (p. 114) with its correct meaning of "shortly," "in a little while."

There is an interesting chapter of 23 pages on Silica in Living Organisms in which there is speculation concerning the role of silicates in the origin of life, and information not summarized elsewhere, so far as the reviewer is aware, on the occurrence of silica in plants and animals.

The book is well printed and nicely bound. It will be a valuable handbook for the information and references contained for those interested in the formation, properties, and uses of colloids of silica and certain of the silicates.

EARL INGERSON,

U. S. Geological Survey, Washington 25, D.C.

NUCLEAR GEOLOGY, edited by HENRY FAUL, John Wiley & Sons, Inc., New York, 1954, 414 pp., \$7.00.

Faul states in the preface that this volume was compiled to introduce graduate students and professional geologists "to a new approach to some questions of the Earth," i.e., the application of nuclear physics to certain geologic problems. The various sections have been written by workers in their respective fields and from this point of view it is up-to-date and authoritative. However, while the essential problems are covered, no attempt has been made to produce an exhaustive treatment of nuclear geology. The author freely admits that stable isotope studies as applied to geologic problems have been omitted because of the rather complete coverage in other books currently being published.

The volume is set up in the form of a symposium, essentially each chapter being contributed by a different author. The first chapter is a brief introduction to nuclear physics, the instruments used, and the techniques of detection and measurement. The explanations are simple and easily understood by the geologist who has had only an introductory course in physics.

The next three chapters treat thorium, uranium, potassium, and the rare gases as found in nature. There is a rather thorough treatment of the distribution of thorium and uranium in igneous, sedimentary, and volcanic rocks, and also in ocean waters and sediments. The discussion of potassium is rather short and is limited to the abundance of potassium in the earth's crust. Chapter 4 is an interesting discussion of helium, argon, and radon as the products of nuclear reactions in nature.

Chapter 5 describes the generations of heat in rocks, evaluation of the abundance data necessary for the calculations, and some theoretical considerations based on our present knowledge.

The next two chapters deal mainly with natural radiation damage. Chapter 6 is a discussion of the damage and changes due to alpha, beta, and gamma rays passing through rocks and minerals, and some of the consequences of this action. Chapter 7 describes the production of liquid and solid hydrocarbons due to the bombardment of gaseous hydrocarbons by alpha particles. Theoretical conclusions based on known organic content of marine sediments are examined.

Chapter 8 describes some of the instruments and techniques used in geophysical prospecting for radioactive ores, and neutron well logging. Chapter 9 is an extensive review of the important methods being used for the determination of geologic age. It is well supplemented with experimental data and a discussion of errors in the methods used. The volume is terminated with a chapter on the origin of the earth. Various recent theories are discussed and arguments for and against various phases are presented.

This book has been amply supplemented with well over 700 references. Its simple presentation, numerous illustrations, and tables of experimental results make it a valuable reference for those geologists who are not steeped in the science of nuclear physics, but who nevertheless want to keep up with the most modern techniques and methods now being applied to geologic problems. It is highly recommended for those "people who pick up rocks and stop to think."

FRANK E. SENFTLE,
U. S. Geological Survey, Washington 25, D.C.

THE PEAKS OF LYELL, by GEOFFREY BLAINEY, Melbourne University Press, Carlton, N. 3, Victoria, and Cambridge University Press, London and New York, 1954. x+310 pages, 18 plates, 5 maps. Price, \$5.00.

This interesting and well-written little book is a history of mining in western Tasmania. It is woven around the story of the Mt. Lyell Mining and Railway Company and is much more concerned with the men who ran the mines and the dividends declared by the companies than with the mineralogy and geology of the deposits. Metallurgical processes are discussed only as they bear on the success or failure of a mining venture.

In the extensive bibliography there are only two papers that deal with the geological setting and mineralogical composition of the ores. Three more recent ones that might have been mentioned are:

Edwards, E. B.: Some observations on the mineral composition of the Mount Lyell copper ores, Tasmania, and their modes of occurrence, *Proc. Austral. Inst. Min. and Met.*, No. 114, pp. 67-110 (1939).

Stilwell, F. L.: Observations on the zinc-lead lode at Rosebery, Tasmania, *Proc. Austral. Inst. Min. and Met.*, No. 94, pp. 43-68 (1934).

Hills, Loftus: A synopsis of the geology of the Lyell District, Tasmania, *Proc. Austral. Inst. Min. and Met.*, No. 66, pp. 129-148 (1927).

EARL INGERSON,
U. S. Geological Survey, Washington 55, D. C.

COALS AND BITUMENS AND RELATED FOSSIL SUBSTANCES. Nomenclature and Classification by S. I. TOMKEIEFF. 122 pp., 3 figures, 3 tables. Pergamon Press Ltd. 242 Marylebone Rd., London N. W. 1, England. 1954. 17s.6d.

This is a valuable little book that seeks to bring a much needed order out of the chaos of names relating to fossil carbonaceous substances, chiefly the coals and bitumens, groups of natural organic substances plagued by an over-exuberant nomenclature and a correspondingly emaciated definitiveness. In addition to compiling a relatively complete, but compact, glossary, Dr. Tomkeieff presents a simple but effective classification of carbonaceous substances (Introduction). Part I, the largest section, is an alphabetical glossary. Appendix 1 is a list of some German, French, and other non-English terms; Appendix 2 is a list of abbreviations relating to the bibliography; and Part II consists of the Synoptic Tables. Both scientific and vernacular terms are included. If the meaning of the term or the approximate composition of the substance is known, the name may be secured by consulting the appropriate synoptic table; conversely if the term is at hand, its definition can be obtained from the alphabetical list.

The book is a valuable reference tool for mineralogists and geologists and workers in allied fields such as mining engineers, fuel technologists and organic chemists.

E. WM. HEINRICH,
University of Michigan, Ann Arbor, Michigan

THE BIRTH AND DEVELOPMENT OF THE GEOLOGICAL SCIENCES, by FRANK DAWSON ADAMS, Unabridged republication, 506 pp., 92 illustrations, Dover Publications, Inc., 1780 Broadway, New York 19, N. Y. 1955. \$1.95 paperbound, \$3.95 clothbound.

In 1938 the first edition of the classic work, *The Birth and Development of the Geological Sciences* by the late Professor Frank Adams was published. Now it has been reissued in unabridged form at a price that makes it readily accessible to students as well as to professional geologists. The typography is legible, and the numerous illustrations are in general clear. The book remains not only the authoritative work on the histories of mineralogy and geology but also offers fascinating reading to any worker in or at the margins of the earth sciences.

Since the original edition was not reviewed in the *American Mineralogist*, at least a listing of the chapter subjects seems desirable in order to acquaint those few unfortunate uninitiates with this remarkable and extraordinarily entertaining account.

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E. WILLIAM HEINRICH,
University of Michigan, Ann Arbor, Michigan

NEW MINERAL NAMES

Nenadkevichite

M. V. KUZ'MENKO AND M. E. KAZAKOVA, Nenadkevichite—a new mineral. *Doklady Akad. Nauk S.S.S.R.*, **100**, 1159–1160 (1955).

The mineral was found as foliated segregations measuring from a few millimeters to $4 \times 2.5 \times 0.4$ cm. Rough faces, taken to be (100), are cut by narrow faces at angles of approximately $41\frac{1}{2}^\circ$ and $46\frac{1}{2}^\circ$. Probably orthorhombic, from the optics. Poorly developed cleavage, (001), was noted under the microscope. The color is dark brown, brown, to rose; it is due in part to impurities of hydrous manganese oxides. Streak pale rose. Luster dull. Hardness about 5. Specific gravity (pycnometer) 2.838 (brown), 2.885 (rose).

Nenadkevichite is optically biaxial, positive, with $\alpha=1.659$, $\beta=1.686$, $\gamma=1.785$, all ± 0.002 (immersion method), $2V=46^\circ$ (Federov stage). The optic axial plane is (001), $X=x$, $Y=z$, $Z=y$. Pleochroism slight, X colorless, Y pale yellow, Z pale rose. Extinction parallel.

Analyses by M. E. Kazakova gave for the brown and rose varieties, respectively: SiO_2 36.72, 37.15; Al_2O_3 0.62, 1.15; TiO_2 9.69, 12.12; ZrO_2 —, —; Nb_2O_5 24.05, 24.61; Fe_2O_3 1.40, 0.80; rare earths 0.25, 0.30; MnO 1.08, 2.90; MgO 0.45, 0.52; BaO 2.75, 1.39; CaO 4.30, 1.75; Na_2O 3.34, 4.16; K_2O 2.68, 2.24; H_2O^+ 8.98, 8.84; H_2O^- 2.36, 2.00; sum 98.67 (given as 99.67 in original M.F.), 99.93%. Spectrographic analysis showed the presence of Be, Zn (medium lines), Cu, Ta, Pb (very weak lines), Ag (traces). The analysis corresponds to $\text{ABSi}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$, where $A = \text{Na, K, Ca, Ba, Mn, Mg}$; $B = \text{Nb, Ti, Fe}$, and both H_2O^+ and H_2O^- are calculated in the formula. The major constituents give (Na, K, Ca) (Nb, Ti) $\text{Si}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$. The mineral is fusible with difficulty to a brownish-black glass. The borax bead is transparent wine-yellow in the oxidizing flame, violet in the reducing flame. The mineral is easily dissolved by sulfuric acid, with difficulty in HNO_3 and HCl .

X-ray powder data by N. N. Sludsko are given. The strongest lines (spacings and intensities) are 3.20 10, 3.10 10, 1.427 10, 1.289 9, 2.49 8, 6.82 7, 2.58 7, 1.705 7.

The mineral occurs between crystals of microcline in a natrolite-albite pegmatite vein in aegirine-lujavrite and genetically associated with poikilitic (hackmanitic) syenite. The locality is not stated (Kola Peninsula? M.F.)

The name is for Konstantin A. Nenadkevich, Russian mineralogist and geochemist.

DISCUSSION: Murmanite has a composition rather similar to that of nenadkevichite, but with $\text{Ti} > \text{Nb}$ (TiO_2 29.51, Nb_2O_5 7.71, Ta_2O_5 0.50%). It is stated to be monoclinic and has n_s 0.05 to 0.08 higher than those of nenadkevichite.

MICHAEL FLEISCHER

Doverite

WILLIAM LEE SMITH, JEROME STONE, DAPHNE D. RISKA AND HARRY LEVINE, Doverite, a new yttrium mineral. *Science*, **122**, No. 3157, p. 31 (1955).

The mineral occurs as brownish-red, irregular aggregates, some as large as one inch in diameter. The aggregates contain very fine-grained doverite, hematite, xenotime, and quartz, and some have rims of bastnaesite. They have non-metallic luster and brownish streak, are brittle with uneven to subconchoidal fracture, and have hardness = $6\frac{1}{2}$, $G = 3.89$. The aggregate is anisotropic with n_s in the range from 1.685 to 1.700.

Analysis of the aggregates gave rare-earth oxides 44.36 (including Ce_2O_3 7.40), ThO_2 1.62, SiO_2 9.70, Fe_2O_3 8.90, CaO 9.80, P_2O_5 8.75, Al_2O_3 0.54, UO_3 0.22, TiO_2 0.75, MgO 0.53; total H_2O 1.35, CO_2 11.75, F 2.87; total 101.14 less ($\text{O} = \text{F}_2$) 1.21, 99.93%. Spectrographic analysis by K. E. Valentine showed Y major, Ce, La, Gd minor, and Dy, Er, Yb, Nd, Pr, Lu, Ho, Tm, and Eu traces. The analysis after deduction of quartz, hematite, and xenotime

corresponds to $\text{YFCO}_3 \cdot \text{CaCO}_3$, the Y analogue of synchisite. Treatment with concentrated HCl leaves a residue of quartz and xenotime. The x -ray pattern is very similar to that of synchisite; the strongest lines are 9.7, 3.53, and 2.78 Å.

The mineral occurs at the Scrub Oaks iron mine at Dover, Morris County, New Jersey. The name is for the locality.

M. F.

Chiklile

S. A. BILGRAMI, Manganese amphiboles from Chikla, Bhandara district, India. *Mineralog. Mag.*, **30**, 633–644 (1955).

The name chiklile is given to an amphibole whose "optical and chemical properties do not resemble closely any known amphibole." Analysis by R. K. Phillips on material air-dried at 105° gave SiO_2 52.66, Al_2O_3 1.75, TiO_2 0.60, Fe_2O_3 18.44, FeO 0.86, MgO 6.29, MnO 2.55, CeO 7.80, Na_2O 7.29, K_2O none, H_2O^+ 1.88; sum 100.12%. Spectrographic analysis shows 0.1% Ba, 0.03% Sr, and small amounts of Cr, Co, Ni, Cu, Zr, and Pb. The analysis gives a formula of the $\text{X}_2\text{Y}_5\text{Si}_8$ type, provided that the calcium is put into the Y position. This is close to an arfvedsonite in composition but the latter has $\text{X}+\text{Y}=8$.

The mineral has sp. gr. = 3.44, $\alpha=1.685$, $\beta=1.700$, $\gamma=1.712$, $\gamma:c=8^\circ$, $2V=82^\circ$. It is deep violet in color, with well developed (100) and (110) forms. Pleochroic from carmine to red. It occurs in pegmatite that cuts Mn ore and muscovite schist at the 60-foot level of the Sitasangi mine, Chikla area, Bhandara district, India. The rare amphiboles winchite, tirodite, and juddite are associated minerals, along with blanfordite, piedmontite, rhodonite, quartz, oligoclase, and microcline.

The name is for the locality.

DISCUSSION: What ambitious mineralogist will earn the gratitude of the profession by compiling, calculating, and classifying all amphibole analyses so that we may have the basis for a rational nomenclature?

M. F.

NEW DATA

Falkmanite

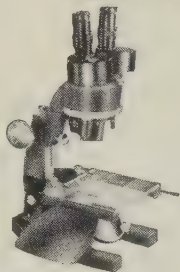
J. E. HILLER, Über den Falkmanit und seine Unterscheidung von Boulangerit. *Neues Jahrb. Mineral., Monatsh.* **1955**, 1–10.

Falkmanite was described by Ramdohr and Ödman in 1939, but was considered by S. C. Robinson in 1948 to be identical with boulangerite (*Am. Mineral.*, **33**, 716 (1948)). Hiller on material from the type locality finds differences from boulangerite in $D.T.A.$ curves, thermoelectric effect, and x -ray constants; he reports for falkmanite $a=15.67$, $b=19.06$, $c=4.02$ Å., $\beta=91^\circ 50'$, probable space group $C_{5h}^{2h}-P_{21}/a$. However, Professor Hiller (letter of April 26, 1955) now states that these data have been found to have been obtained on a sample of jamesonite (the x -ray data agree with those of Berry on jamesonite) and he concludes—"da ich nunmehr der Ansicht von S. C. Robinson anschliessen muss, dass der Falkmanit tatsächlich ein Phantom ist."

M. F.

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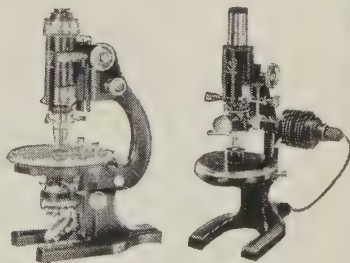
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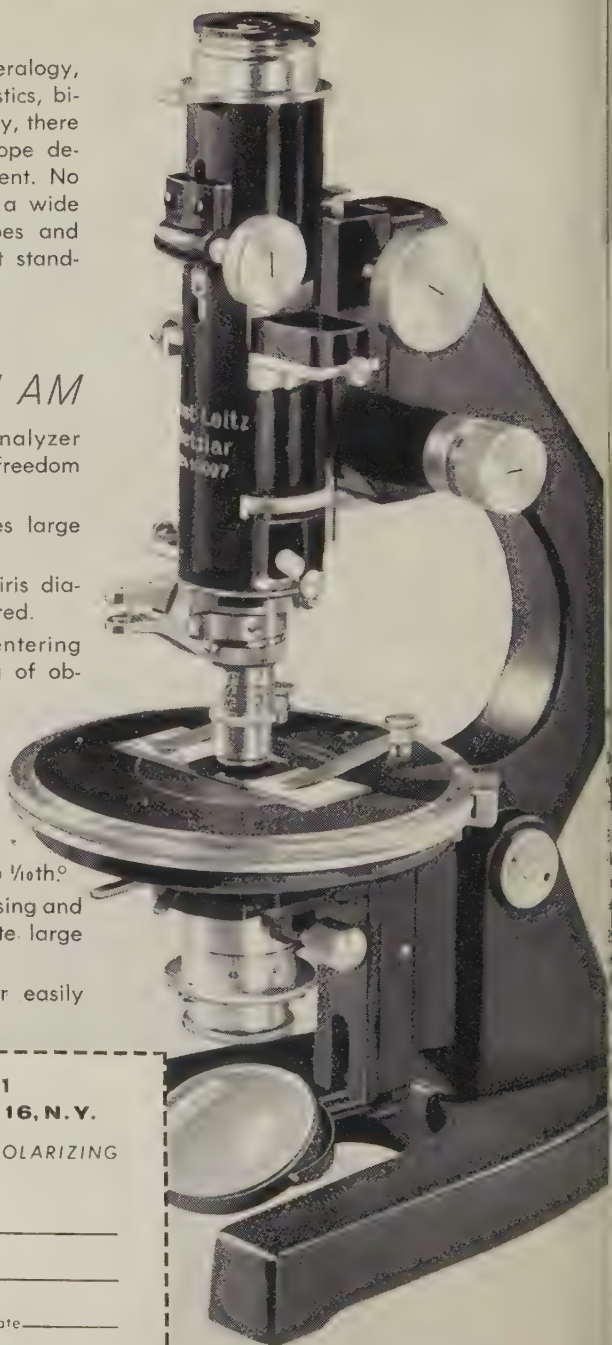
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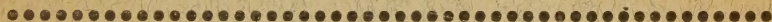
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